

1950

# Phase studies of uranium-zirconium alloys

David Peterson  
*Iowa State University*

Follow this and additional works at: <https://lib.dr.iastate.edu/rtd>

 Part of the [Physical Chemistry Commons](#)

---

## Recommended Citation

Peterson, David, "Phase studies of uranium-zirconium alloys" (1950). *Retrospective Theses and Dissertations*. 15121.  
<https://lib.dr.iastate.edu/rtd/15121>

This Dissertation is brought to you for free and open access by the Iowa State University Capstones, Theses and Dissertations at Iowa State University Digital Repository. It has been accepted for inclusion in Retrospective Theses and Dissertations by an authorized administrator of Iowa State University Digital Repository. For more information, please contact [digirep@iastate.edu](mailto:digirep@iastate.edu).

# NOTE TO USERS

This reproduction is the best copy available.

**UMI<sup>®</sup>**



**PHASE STUDIES OF URANIUM-ZIRCONIUM ALLOYS**

by

**David Peterson**

**A Dissertation Submitted to the  
Graduate Faculty in Partial Fulfillment of  
The Requirements for the Degree of  
DOCTOR OF PHILOSOPHY**

**Major Subject: Physical Chemistry**

**Approved:**

Signature was redacted for privacy.

**In Charge of Major Work**

Signature was redacted for privacy.

**Head of Major Department**

Signature was redacted for privacy.

**Dean of Graduate College**

**Iowa State College**

**1950**

UMI Number: DP12906

### INFORMATION TO USERS

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleed-through, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.

**UMI<sup>®</sup>**

---

UMI Microform DP12906

Copyright 2005 by ProQuest Information and Learning Company.

All rights reserved. This microform edition is protected against unauthorized copying under Title 17, United States Code.

ProQuest Information and Learning Company  
300 North Zeeb Road  
P.O. Box 1346  
Ann Arbor, MI 48106-1346

6D181.07

- ii -

1176-129

P492P

## TABLE OF CONTENTS

	Page
I. INTRODUCTION . . . . .	1
II. HISTORICAL . . . . .	5
III. EXPERIMENTAL . . . . .	8
A. Preparation of Alloys . . . . .	8
B. Thermal Analysis . . . . .	17
C. Microscopic Examination . . . . .	23
D. X-Ray Examination . . . . .	26
E. Chemical Analysis . . . . .	27
IV. PRESENTATION OF DATA . . . . .	31
A. Thermal Data . . . . .	31
B. Microscopic Examination . . . . .	40
C. X-Ray Diffraction Data . . . . .	73
D. Hardness and Working Properties . . . . .	79
E. Discussion of Alloy Preparation . . . . .	83
V. SUMMARY . . . . .	88
VI. BIBLIOGRAPHY . . . . .	89
VII. ACKNOWLEDGMENTS . . . . .	91

T12177

## I. INTRODUCTION

There is perhaps no more useful tool in the understanding and predicting of the behavior of an alloy of two metals or the behavior of two metals in intimate contact than a phase diagram of the binary system which they form. The data which is compiled in the study of a binary system can thus be expressed concisely, quantitatively and in a universal graphical form which can be readily interpreted. This investigation had as its object the experimental determination and compilation of data from which a phase diagram could be constructed for the uranium-zirconium binary temperature-composition system and the determination of such other properties of uranium-zirconium alloys as appeared of interest. A secondary objective was the development of a method of preparing these alloys which would be useful in the case that some of these alloys should have desirable properties.

In the field of nuclear fission and its engineering aspects little was known of the physical and chemical characteristics of many of the materials which were found to have useful nuclear properties. Some of them, such as uranium and thorium, were classified among the rare metals and were considered laboratory curiosities. Much has been learned in the last ten years of the physical and metallurgical properties of uranium but there are many problems yet to be studied. The importance of the uranium-zirconium alloy system is a result of the fission properties of uranium and of the

physical and nuclear properties of zirconium. Zirconium has a low cross section for slow neutron capture and in addition has strength and corrosion resistance which make it a desirable pile construction material. Since any fission pile built of zirconium would contain uranium, perhaps in close contact or even alloyed with the zirconium, a knowledge of the phase system formed by these two metals would be essential. Not all of the properties of an alloy can be exactly predicted from the phase diagram. Properties such as the hardness, ductility and corrosion resistance are often of prime importance and must be specifically studied in order to provide the necessary additional quantitative information. Equally as important as the knowledge of the properties of an alloy is a method for the production of that alloy in a desired form. All of this information would be very helpful to physicists and pile engineers.

Uranium is a heavy, hard metal with a silvery luster which rapidly darkens in air to a golden color and then to a blue or brown. According to the Project Handbook,<sup>1</sup> the metal melts at  $1132^{\circ}\text{C}$  and has three allotropic forms. From room temperature to  $660^{\circ}\text{C}$ , the stable form is alpha uranium which has an orthorhombic lattice with four atoms per unit cell and  $a:b:c$  equal to  $2.852:5.865:54.945$  angstroms. Beta uranium exists from  $660^{\circ}\text{C}$  to  $770^{\circ}\text{C}$  and has a complex structure which recent work at the Knolls Laboratory<sup>2</sup> has established as being either orthorhombic or monoclinic with sixty atoms per unit cell. Above  $770^{\circ}\text{C}$  to the melting point, uranium has a body centered cubic structure with a lattice constant equal to



3.48 angstroms. The hardness of cast uranium of usual pile purity is RB 88 - 90. The observed density varies from 18.7 to 19.05 grams per cubic centimeter. A survey of published phase diagrams of uranium reveals no elements which are appreciably soluble in alpha uranium but solubility in beta and gamma uranium is often found. This agrees with certain theoretical predictions made by Rayner<sup>3</sup> on the basis of the various structures of uranium, its electronegativity and number of valence electrons.

Boulger<sup>4</sup> reports the following properties of zirconium in a review article covering the metallurgy of zirconium. Zirconium is a silvery metal which does not tarnish in air at room temperatures. It is quite soft and ductile when pure but is very difficult to prepare in a highly pure form. It occurs in nature associated with from one to three per cent of hafnium. Due to the very close chemical similarity of these two elements which makes their separation very difficult, most zirconium contains that amount of hafnium. However, it is expected that the physical properties of hafnium-free zirconium will not be appreciably different from those of the usual material. For pile purposes the hafnium must be removed since it has a very high cross section for capture of slow neutrons. The melting point of zirconium is reported as  $1830^{\circ}\text{C} \pm 40^{\circ}\text{C}$ . Zirconium has a hexagonal closest packed structure at temperatures up to  $863^{\circ}\text{C} \pm 3^{\circ}\text{C}$ . The lattice constants for the hexagonal form are,  $a = 3.228$  angstroms and  $c = 5.120$  angstroms. The density of alpha zirconium at room temperature is 6.50 grams per cubic centimeter.

The beta form is stable from  $863^{\circ}\text{C}$  to the melting point and Burgers<sup>5</sup> has reported that the structure is body centered with the lattice constant equal to 3.61 angstrom at  $867^{\circ}\text{C}$ . The lattice constant extrapolated to room temperature to compare with the lattice constant of gamma uranium would probably be about 0.5 per cent smaller than the value of  $867^{\circ}\text{C}$ . The hardness, ductility and other mechanical properties vary with the purity of the metal, particularly with the amount of oxygen, nitrogen and carbon which is present.

## II. HISTORICAL

A survey of the literature indicated that prior to 1943, no work had been reported on alloys of uranium with zirconium. Since both metals were quite rare and expensive this is not unexpected. The only available source of information on these alloys is in the classified reports of the Atomic Energy Commission. A complete survey and accurate appraisal of the work which has been reported is rather difficult because it is included with other information in a large number of progress reports. These reports cover the work done in a certain fixed period of time and are, as a result, quite fragmentary and do not summarize the work done previously. A review article by Buzzard and Cleaves<sup>6</sup> on the binary alloys of uranium gives a resume of the work done on this system up to 1948 and includes a bibliography of classified reports dealing with this subject.

The first information to appear on alloys of uranium and zirconium was reported by Seybolt<sup>7,8,9</sup>. An investigation was made of the effect of various alloying metals including zirconium, on uranium metal. A few alloys were prepared containing principally uranium and their hardness and microstructures studied. On the basis of this preliminary work, it was decided that zirconium did not greatly improve the properties of uranium and the study of uranium-zirconium alloys was discontinued.

The first systematic investigations of the uranium-zirconium alloy diagram were made by Kaufman<sup>10,11,12,13,14,15,16,17,18</sup> and

co-workers starting in 1944. Results of this work indicated that the melting point of uranium was raised by the addition of zirconium. The beta to gamma transition was lowered to  $700^{\circ}\text{C}$  at 6 atomic per cent zirconium and then remained constant with further increase in zirconium content. The alpha to beta transition was raised to  $675 - 700^{\circ}\text{C}$  by additions of zirconium. Attempts to retain gamma uranium by quenching zirconium-uranium alloys from  $1000^{\circ}\text{C}$  were unsuccessful. The corrosion resistance of these alloys was studied and the alloys quenched from above the beta-gamma transformation showed better corrosion resistance than pure uranium or as-cast alloys. Solubility of uranium in zirconium to the extent of about 10 per cent was indicated but the report did not indicate whether this solubility was in alpha or beta zirconium. An intermetallic compound was postulated.

Following later work by Kaufmann<sup>19,20,21,22,23,24</sup> and co-workers, they have reported complete solid solubility between gamma uranium and beta zirconium. Examination by X-ray diffraction of the alloys from 49 per cent to 69 per cent uranium has shown a body centered cubic phase in samples quenched from above  $600^{\circ}\text{C}$  and a body centered tetragonal phase in alloys quenched from  $600^{\circ}\text{C}$  and lower temperatures. The lattice constant of the body centered cubic phase was found in three alloys of varying composition to be approximately  $3.55 \text{ \AA}$ , which is intermediate between beta zirconium and gamma uranium. These alloys were prepared by vacuum melting swaged crystal bar zirconium and uranium in graphite crucibles. The

melt was stirred with a graphite stirrer to insure homogeneity of the alloys. Solubility of uranium in alpha zirconium of 3 to 5 per cent was reported but the temperature to which this applied was not specified.

A group of workers at the Chicago Metallurgical Laboratory<sup>25,26,27,28</sup> also began an investigation of the uranium-zirconium phase diagram in 1944. They have reported two horizontals in the diagram, one at 675 and one at 605° C for uranium-rich alloys. A martensitic microstructure was observed in uranium-rich samples quenched from above 700° C. The existence of two eutectoids was postulated. The alloys were prepared by melting uranium and zirconium in beryllia crucibles. These alloys and also ternary alloys containing columbium, uranium and zirconium were examined for corrosion resistance. The zirconium alloys had somewhat better corrosion resistance than pure uranium but the addition of columbium had a greater effect in improving corrosion resistance.

At the present time, several laboratories are working on uranium-zirconium alloys as fuel element construction materials. Among these are Battelle Memorial Institute<sup>29</sup>, Knolls Atomic Power Laboratory and Sylvania Electric Company. However, in connection with the program of the U. S. Atomic Energy Commission, only at the Massachusetts Institute of Technology and at the Ames Laboratory are investigations of the complete binary phase diagram under way.

### III. EXPERIMENTAL

Alloys of uranium and zirconium were produced by bomb reduction and by arc melting. They were then studied by thermal analysis and other pyrometric methods to investigate the solid state transformations and the liquidus and solidus temperatures. Microscopic examination was used to determine the number of phases present in the various regions and X-ray diffraction was used to identify the phases. Information was also obtained on the hardness, ductility and purity of these alloys.

#### A. Preparation of Alloys

One of the greatest difficulties in studying alloys of uranium and zirconium is the preparation of homogeneous alloys without gross contamination of the sample. Uranium is a very active metal which reacts readily with oxygen, nitrogen, water vapor and many other gases at relatively low temperatures. However, it does not dissolve appreciable amounts of oxygen and can easily be melted under vacuum or in a noble gas atmosphere in beryllia or zirconia crucibles. Pure zirconium is quite inert to reaction with oxygen, nitrogen and water vapor at low temperatures but is used as a getter at elevated temperatures. DeBoer<sup>30</sup> has reported that zirconium will dissolve up to 40 atomic per cent oxygen and up to 20 atomic per cent nitrogen. The presence of much smaller amounts of such impurities in solid solution in an alloy would no doubt vitiate any results and

make it difficult to determine the true nature of the binary metal alloy. The only satisfactory refractory known at present in which zirconium may be melted without oxygen pick up is graphite. Melting in graphite results in from 0.1 to 0.5 per cent carbon contamination but this is somewhat less serious since the solubility of carbon in alpha zirconium appears to be quite low, probably about 0.1 per cent or less.

The preparation of uranium-zirconium alloys by melting the two metals in graphite results in the introduction of more carbon than in the melting of zirconium alone in carbon since the solubility of carbon in liquid uranium is quite large at temperatures above 1400° C. All of the alloys which were prepared by melting in graphite crucibles were very hard and a phase which was identified as carbide appeared in the microstructure in large amounts. Several alloys were melted in beryllia crucibles and this appeared to be satisfactory for alloys which melted below 1450° C. Above this temperature the reaction of the alloy with the crucible became very severe and this method could not be used. Due to the difficulty of analysing uranium-zirconium alloys for beryllium, the decision was made to eliminate beryllia crucibles even for the low zirconium alloys since there would be no way of determining the amount of contamination.

An arc melting apparatus which melted metals in a water cooled copper crucible was used to melt Bureau of Mines sponge with uranium metal. This equipment was built here and became available late in this investigation. A DC arc was used from a water-cooled tungsten

electrode to the metal contained in a water-cooled copper crucible. The voltage was about 40 volts and 400 amperes passed through the arc. The tungsten electrode was made negative and very little tungsten was volatilized or transferred to the melt. The chamber in which the melting was done was evacuated to 20 microns and flushed with purified helium. This was done three times before the metal was melted. Bureau of Mines sponge zirconium was melted by this method to produce massive metal which had a Rockwell A hardness of 38 to 42. Spectrographic analysis indicated that the copper content of the melted metal was below 400 P.P.M. and no tungsten was detected. It was necessary to remove the magnesium and other volatile substances from the sponge zirconium before it was melted to avoid bubbling and splattering of the melt and disruption of the arc. This was done by heating the sponge zirconium under vacuum to 1400° C. The uranium-zirconium alloys produced in this apparatus were melted and held liquid for several minutes. They were then turned over and remelted to insure homogeneous distribution of the two components. These alloys were very clean and shiny after being melted and the top surfaces showed large macrocrystals. The microstructures were quite clean and very little carbide could be seen. Analytical results indicated that the alloys prepared by this method were sufficiently homogeneous for most metallurgical purposes.

Powdered uranium in a very finely divided form is easily prepared by formation and subsequent decomposition of the hydride and may be handled if suitable precautions are observed. If a good grade



of fine zirconium powder had been available, powder metallurgy techniques probably could have been used more extensively in alloy preparation. The method for preparing zirconium powder by formation and then decomposition of the hydride involves heating the powder under vacuum to 600 - 700° C. In view of the reactive nature of zirconium, it was doubtful if this method would be suitable for the preparation of very pure zirconium powder in small quantities. Since this early work was done, reports have been published by Angier and Hausner<sup>31,32</sup> which describe a method for producing zirconium powder and powdered zirconium hydrides. The zirconium powder produced was fine enough to pass a 200 mesh screen and was only slightly less pure than the original metal. A number of alloys were prepared by pressing and sintering uranium powder with zirconium powder which had been prepared by the hydride process or by sawing massive zirconium and collecting the saw dust under CO<sub>2</sub>. These samples were then annealed in graphite crucibles in graphite heaters lined with zirconium or molybdenum sheet. A considerable amount of difficulty was encountered in reaching equilibrium and the alloys usually were contaminated by carbon and oxygen before they were sufficiently annealed. This method was discarded as involving entirely too many experimental difficulties.

A fourth method of preparing alloys is the simultaneous reduction to the metallic state of a mixture of compounds of the two elements. Since methods were known for producing both uranium metal and zirconium metal, this approach was tried. A method for preparing

uranium metal on a small scale by bomb reduction was described by Spedding<sup>33</sup> and a process for preparing zirconium metal by bomb reduction has been reported by Walsh<sup>34</sup> in a recent paper.

The alloys were prepared by bomb reduction of uranium tetrafluoride and zirconium tetrafluoride using calcium as the reductant. Iodine was used as a booster to furnish additional heat and the resulting calcium iodide tends to lower the melting point of the slag. The reduction was carried out in a 2 1/2 inch inside diameter bomb which was 12 inches long. A cross section view of the bomb is shown in Figure 1. The bomb was made from 2 1/2 inch standard steel pipe. One end was closed by welding in a plug and the other was closed by means of a cast iron pipe cap.

It is necessary to line the bomb with a refractory to prevent contamination of the charge by metal from the walls of the bomb and to protect the steel from the hot slag and metal products of the reduction. This liner, in the case of uranium reductions, usually consists of magnesium oxide or of electrically fused dolomitic oxide. For the production of these alloys presintered dolomitic oxide crucibles were used as liners for alloys containing ten per cent zirconium and less. The inside diameter of these crucibles or liners was 2 inches, the outside diameter 2 3/8 inches and the length 11 inches.

Since zirconium has such a powerful affinity for oxygen, there was doubt that high zirconium alloys could be prepared sufficiently free of oxygen in dolomitic oxide liners. Some high zirconium alloys

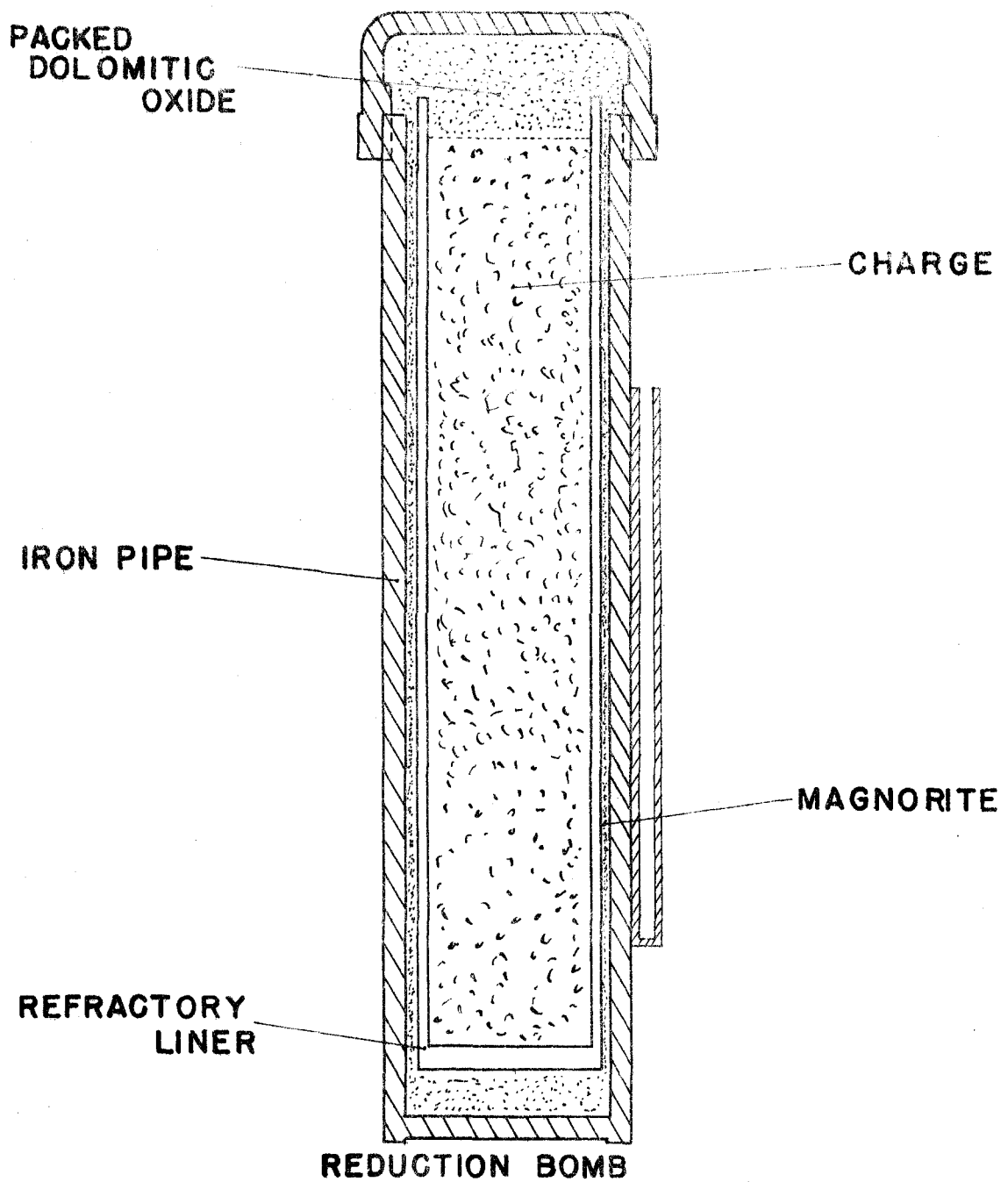


Figure 1 - Cross section view of reduction bomb.

and pure zirconium were prepared by reduction in dolomitic oxide liners, but these alloys were very hard and quite brittle. The pure zirconium prepared in dolomitic oxide was also very hard, quite brittle and the microstructure consisted of long needles rather than the polyhedral grains typical of a pure metal. The use of graphite liners was obvious since zirconium does not dissolve carbon as readily as it dissolves oxygen. A sample of zirconium prepared by using graphite liners was found to be softer than metal produced in dolomitic oxide liners and could be given 50 per cent reduction in area by cold rolling. This metal had a polyhedral grain microstructure and seemed quite free of inclusions and impurities. The graphite liners which were used were 2 inches inside diameter, 2 3/16 inches outside diameter and 11 inches long. They were machined from AGR electrode grade graphite rods obtained from National Carbon Company.

The liner of either dolomitic oxide or graphite was placed in the bomb with sufficient coarse magnesium oxide below so that the top of the liner projects 1/8 inch from the open end of the bomb. Magnesium oxide was then poured into the annular space between the liner and the bomb wall to hold the liner in place and to provide additional insulation. The charge for the alloys was prepared by weighing out the proper amounts of uranium tetrafluoride, zirconium tetrafluoride, calcium metal and iodine. The uranium tetrafluoride was obtained from Mallinkrodt Chemical Company and analysed above 99 per cent uranium tetrafluoride. The zirconium tetrafluoride was

prepared by several different methods. These are described by Walsh in the report on bomb reduction in considerable detail. Most of the alloys were prepared from zirconium tetrafluoride which had been purified by sublimation under vacuum. The zirconium tetrafluoride was ground to pass a 100 mesh screen by a small hammer mill. The iodine was USP XIII Resublimed Crystals obtained from Mallinkrodt Chemical Company. Since the iodine is molten at temperatures below that at which the bomb ignites grinding was unnecessary. The calcium used was purified by distillation at the Ames Laboratory and was of very high purity. The calcium was ground in a mill equipped with chopping blades to pass a 10 mesh screen and was screened to remove the material which passed 80 mesh since this fine material contained a large amount of oxide.

The relative amounts of uranium tetrafluoride and zirconium tetrafluoride which were used in the charge were determined by the alloy composition desired. The weight of the alloy biscuit which could be produced varied from 340 grams for uranium-rich alloys to 160 grams for zirconium-rich alloys. A 15 per cent excess of calcium was used over the amount required to react with all the uranium and zirconium fluorides and the iodine. The quantity of iodine used varied from 63 grams for uranium-rich alloys to 380 grams for the zirconium-rich alloys.

This charge was mixed by rolling and tumbling in a square-form two quart bottle. The fluorides and calcium were thoroughly mixed before the iodine was added and the final mixing done. This procedure

was followed to reduce the reaction between iodine and calcium during mixing. The mixed charge was then poured into the bomb liner. Argon was introduced through a tube which projected to the bottom of the bomb liner to displace the air from the bomb and charge. The top of the charge was packed slightly before the liner was closed.

A graphite lid was placed on the bomb liner and dolomitic oxide packed on top to hold the lid in place. The bomb was then closed by means of the pipe cap and sealed with a pipe sealing compound to prevent the escape of iodine. The charge was ignited by heating the bomb in a gas fired furnace which was held at a temperature of about 700° C. After the reaction was complete, the bomb was cooled to room temperature and the biscuit of metal or alloy removed. The slag adhering to the biscuit was removed by chipping with a hammer followed by leaching with water and then with dilute nitric acid. The yields of metal that collected at the bottom of the bomb generally decreased as the percentage of zirconium in the alloy increased and varied from 98 per cent to 50 per cent. The composition of the alloy found by chemical analysis was usually very close to the ratio of the elements in the charge.

The alloys were given a homogenizing anneal under vacuum before being studied by thermal analysis, microscopic examination and X-ray phase determination. The alloys containing less than 15 per cent zirconium were homogenized by heating at 900° C for 16 to 24 hours in a resistance furnace. The alloys containing higher percentages of zirconium were annealed at a temperature estimated to be several

hundred degrees below the melting point of the alloy for about one hour. This annealing was done in a graphite crucible heated by a 20 kilowatt mercury arc induction furnace. The heating was done under vacuum and the temperature was observed by means of an optical pyrometer. The graphite crucible was lined with zirconium sheet which completely enclosed the sample of metal. This was done to prevent contamination of the alloy by oxygen, nitrogen and carbon. During the course of the investigation, it was found that the alloys were quite homogeneous as they came from the bomb and that annealing at 900° C was sufficient for alloys of all compositions.

#### B. Thermal Analysis

The melting points of alloys with more than five per cent zirconium was too high to allow determination of the liquidus and solidus temperatures by thermal analysis. However, the solid state transformations were sufficiently rapid so that thermal analysis was extremely useful in the determination of phase boundaries in the solid state. These transformations were found to be subject to considerable super cooling and could be studied with much greater reproducibility and more information could be obtained by the use of heating curves rather than cooling curves.

To provide a constant heating rate and thus make the curves simpler and more sensitive, an apparatus was designed and built which maintained a constant temperature differential between the furnace and the sample. A photograph of this equipment is shown in

Figure 2 and a schematic diagram is shown in Figure 3. The heating was done by a 750 watt electrical resistance furnace which accommodated a 1 inch outside diameter quartz tube. The power for the furnace was supplied by a 110 volt Variac. The furnace was controlled by a Brown Electronik circular scale potentiometer which was connected to a Modutrol motor. This potentiometer was fed the output of a differential thermocouple of chromel-alumel-chromel. One junction was located inside the sample and the other was just outside the quartz tube. Thus the potentiometer read the temperature differences between the sample and the furnace and was set to control this difference so as to produce the desired heating rates. The Brown potentiometer supplied an impulse to the Modutrol motor, which was coupled to the shaft of the Variac, such that if the temperature differences were too small, the Variac would be turned up and if the difference was too large, the Variac would be turned down. The temperature of the sample was recorded by a Brown Electronik recording strip chart potentiometer which was connected to the thermocouple inside the sample. Since a potentiometer is a null point instrument, it was possible to have two potentiometers connected with the same thermocouple circuit. The possibility of interference between the two potentiometers was considered and tests were made which proved that each potentiometer had no effect on the other after they had reached the balance point. An insulated cold junction consisting of a thermos bottle of water was used to provide a fairly constant cold junction correction.





Figure 2 - Thermal analysis furnace.

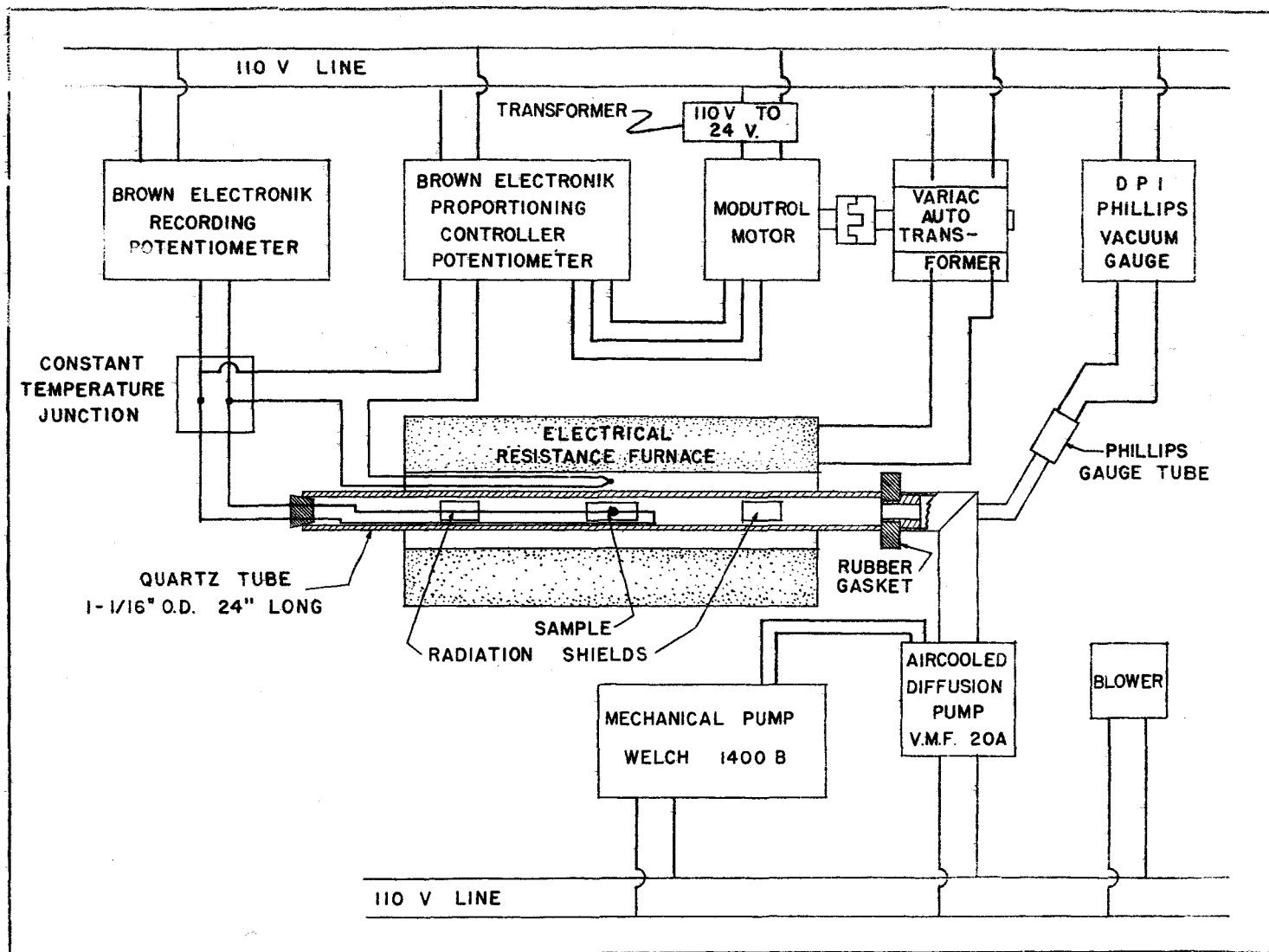


Figure 3 - Schematic drawing of thermal analysis furnace.

The alloy sample was placed in the 1 inch outside diameter quartz tube shown in Figure 3. This tube was evacuated by a 20 liter per second capacity air cooled oil diffusion pump and a Welch Duoseal 1400 mechanical backing pump. The vacuum was measured by means of a Phillips gauge and at the beginning of a run was always lower than 0.02 microns. During the initial heating period the pressure would rise to about 0.04 microns but would fall to below 0.02 microns after the maximum temperature had been reached. The samples heated under this vacuum showed very little oxidation even after heating for 48 hours. The heating rate obtained with this apparatus was very nearly linear from 300° C to 800° C and any significant thermal arrests up to 900° C could have been readily detected. The linear curve and constant heating rate made the detection of an arrest quite easy and made possible an estimate of the magnitude of the heat effect.

The solidus and liquidus temperatures of alloys up to 5 per cent zirconium were determined by running cooling curves using chromel-alumel thermocouples. The sample was placed in a beryllia crucible inside a graphite heater. The heating for this part of the investigation was done under vacuum by an induction furnace. The graphite heater was insulated well enough to give a suitable cooling rate when the power was shut off. The samples were heated above 1300° C and allowed to cool. The temperature was recorded on a Leeds and Northrup Micromax recording potentiometer.

The solidus and liquidus temperatures of alloys containing more than 5 per cent zirconium were above the range of the chromel-alumel thermocouple so it was necessary to use other means of obtaining these temperatures. The method which was used consisted of heating a sample of the alloy by passing a high amperage current through it and observing the appearance of liquid by an optical pyrometer. A complete description of the method is reported by Chiotti<sup>35</sup> with details of the equipment. The samples were bars approximately 1/4 inch by 1/4 inch by 2 inches. A small hole 1/8 inch deep was drilled in the center of the bar with a number 69 drill to provide black body conditions for temperature measurement. The sample was clamped between water cooled copper electrodes in a vacuum chamber and current passed through the sample. By means of an optical pyrometer, the hole in the sample was observed as the temperature was increased and the temperature at which the first sign of liquid metal appeared was observed for different compositions. This temperature must lie between the liquidus and solidus temperatures. The specimen was observed through a glass window in the top of the vacuum chamber and the observed temperature was corrected for the absorption due to the glass by means of a table prepared by Forsythe.<sup>36</sup> The apparatus was evacuated by a Cenco Hypervac 23 mechanical vacuum pump to about one micron before the heating was started. Due to evolution of gas by the sample the pressure would rise above 200 microns during the first heating of the sample and then fall to about 15 to 20 microns by the time the melting point was reached. Most of the

samples were only slightly discolored during heating and the amount of oxidation in these cases was probably rather small.

### C. Microscopic Examination

Since there are several phase transitions in the solid state, it was necessary to anneal and quench a large number of alloys to determine the extent of the various phase fields. The furnace which was used for thermal analysis was also used for annealing and for heating samples to be quenched. The controller potentiometer was connected to the thermocouple inside the quartz tube and could be set to control at any temperature from 400° C to 925° C. The variation in temperature as indicated by the potentiometer was less than plus or minus two degrees centigrade at all temperatures and irrespective of line voltage fluctuations. The samples were first heated to 900° C for 16 to 24 hours to establish equilibrium at that temperature. They were then cooled to just below the quenching temperature and held for several hours and then reheated to the desired temperature and held again for 6 to 24 hours before quenching. By following this schedule, it was hoped that the microstructure would be representative of equilibrium conditions and the hysteresis in phase transitions especially as observed on cooling would be reduced. The samples were quenched by opening and tipping the quartz tube and allowing the samples to fall into a container of water. The examination of the quenched samples indicated that the quench in all cases succeeded in preserving the microstructure.

The samples were prepared for microscopic examination as follows. The specimen was mounted in bakelite and rough ground on a medium grit vitrified wheel. The next step was grinding on wet or dry silicon carbide disks without using a lubricant or coolant. The grinding was started on a number 320 grit wheel and was followed in order by numbers 400, 500 and 600. The sample was then polished on a soft cloth wheel using a suspension of 400 grit silicon carbide powder in a soap solution.

Etching of many of the alloys was very difficult due to very finely dispersed microstructure formed by eutectoid precipitation and to the very chemical resistant properties of some of the quenched samples. The alloys containing up to ten per cent zirconium were all etched electrolytically using a bath of eight parts reagent grade orthophosphoric acid, five parts ethyl alcohol and five parts ethylene glycol. The potential, current density and time had to be adjusted differently for almost every sample. The voltages used varied from 2 volts up to 40 volts, the current density was fixed by the resistance of the bath and the surface of the sample and the time was usually 30 to 60 seconds. Higher voltages were necessary to etch quenched samples that were one phase as compared to two phase samples.

Alloys containing more than ten per cent zirconium and also pure zirconium could be etched with a mixture of one part concentrated nitric acid and two parts of distilled water saturated with sodium tartrate and sodium fluosilicate. This nitric acid base

etching solution was used by swabbing the sample with a cotton applicator filled with the solution. The etching time necessary varied from 15 seconds to several minutes. The best results were obtained by etching the sample quite heavily, repolishing on the cloth wheel with number 400 grit silicon carbide suspension and then etching to bring out the desired structural details. This treatment seemed to remove the cold worked metal left by grinding the sample and made the microstructures much sharper and increased the amount of detail which could be observed. This was a very satisfactory etching solution for most of the alloys in this system and worked quite well on pure zirconium and other alloys of zirconium. The action was sufficiently slow to allow the progress of the etching to be observed and stopped at the proper time. The contrast between various phases was quite satisfactory and could be increased by increasing the etching time. No dark or obscuring film of reaction products was left on the surface and none of the phases present, including zirconium carbide, were unduly etched away. For alloys containing more than ninety per cent zirconium it was possible to use an etching solution consisting of one part of 48 per cent hydrofluoric acid in nine parts of water. This was a satisfactory etch for pure zirconium but its action is extremely rapid and often results in surface irregularities and pitting of the sample with almost complete destruction of the zirconium carbide which was usually present. A few of the high zirconium alloys which did not

etch well with the nitric acid base etching solution were etched with this hydrofluoric acid etching solution.

#### D. X-Ray Examination

The X-ray powder patterns of these alloys at room temperatures were obtained on a 11.4 cm diameter Debye-Scherrer camera using filtered copper radiation. The camera was made by North Americas Phillip and used an unsymmetrical film according to the Straumanis technique which requires no camera calibration. In general samples were prepared by quenching massive pieces of single phase alloys. Filings were then taken from these quenched pieces and were annealed at 560° C in a quartz capillary to remove strain. The oxygen and nitrogen were removed from the capillary, after it was sealed, by heating a small strip of zirconium sheet which was placed in one end of the capillary. After the above annealing the samples were allowed to cool in the furnace to room temperature. The filings were then removed from the quartz capillary and mounted by the use of vaselene on a glass fiber about 0.005 inches in diameter. The glass fiber was then positioned in the powder camera and the diffraction pattern recorded. The usual exposure time was 6 hours with 20 milliamperes passing through the X-ray tube at a potential 35 kilovolts.

A number of attempts were made to determine the crystal structure of these alloys at elevated temperatures. Massive samples were quenched from high temperatures and the X-ray powder patterns of the



unannealed filings obtained from these samples. Also, filings were in quartz tubes and quenched from high temperatures into water and the crystal structure studied. Both of these methods failed to give any information about the crystal structure of the alloys at higher temperatures as the samples transformed in spite of being quenched and only alpha uranium and alpha zirconium were found. A number of attempts to use a high temperature camera built by Otto Von der Heyde were made. This was a 5.7 centimeter diameter powder camera with a small electrical resistance heater around the sample. The sample consisted of filings of the alloy enclosed in a small, thin quartz capillary. Lindemann glass capillaries could not be used because of the temperatures involved. Due to mechanical difficulties with the camera and furnace and to the reactivity of the metal samples, no satisfactory pictures of these alloys were obtained at elevated temperatures.

#### E. Chemical Analysis

The alloys of uranium and zirconium were analysed chemically to check the composition of the alloys and to find the amounts of impurities which were present. The impurities which were analysed for were iron, nitrogen and carbon. The oxygen content of these alloys was not determined since the rather elaborate equipment necessary for this determination was not available. Hafnium was present in amounts of about 2 weight per cent of the zirconium and was assumed to have little influence on the alloys of zirconium and

uranium. Other elements would have been present in amounts of less than 500 parts per million and would not be expected to materially affect the metallurgical properties of the alloys.

The samples for uranium and zirconium analysis were usually single massive pieces due to the difficulty encountered in drilling or grinding the alloys. The samples were treated with concentrated nitric acid in a platinum dish until a black residue remained. This residue was dissolved by adding hydrofluoric acid and then both the nitric acid and hydrofluoric acid were removed by fuming strongly with sulfuric acid. The solution was cooled and diluted with water in a volumetric flask.

The determination of uranium was completed by pipetting an aliquot containing 0.4 to 0.5 grams of uranium from the solution containing the sample. This aliquot was passed through a Jones reductor which reduces the uranium to three and four valent uranium. The three valent uranium was oxidized to four valent uranium by bubbling air through the solutions. The uranium was then titrated with standard sulfatoceric acid solution, using ferroin indicator, to a light blue green end point.

For the determination of zirconium, an aliquot containing approximately 0.2 grams of zirconium was taken. This was evaporated to dryness to remove sulfuric acid, which causes low results if present in more than small amounts. Ten milliliters of concentrated hydrochloric acid were added and the solution diluted to 100 milliliters. After the addition of 30 grams of mandelic acid to this

solution it was heated to boiling for thirty minutes. The precipitate was filtered, ignited and finally weighed as zirconium dioxide.

The amount of iron in these alloys was determined by a colorimetric method using 1,10 phenanthroline. The sample was dissolved by hydrofluoric acid in a platinum dish and then fumed with sulfuric acid for one half hour to remove all the fluoride ion. The solution was diluted to volume, an aliquot was taken and the iron reduced to ferrous iron by hydroxylamine hydrochloride. The 1,10 phenanthroline reagent and a solution of tartaric acid were added and the pH raised to 5 - 7 with ammonium hydroxide. The per cent light transmission at 515 millimicrons was determined on a Coleman spectrophotometer. The amount of iron was determined from a previously prepared standard curve. A portion of the original solution was used as the reference solution since uranium forms colored solutions which would otherwise interfere in the determination.

The determination of nitrogen was done by a modified micro Kjeldahl method. The sample was dissolved in hydrofluoric acid and fumed with sulfuric acid. The standard micro Kjeldahl procedure was then followed to complete the analysis.

A slight modification of the standard combustion method of determining carbon was necessary for a number of the high zirconium alloys. The determination was done by burning a sample of turnings in oxygen, absorbing the  $\text{CO}_2$  in an ascarite tube and observing the gain in weight. The alloys which contained a large percentage of uranium burned smoothly and completely. However, the alloys which

were primarily zirconium had to be mixed with aluminum powder to prevent the formation of an adherent oxide coating which prevented complete combustion. By this modification, complete combustion of the alloys and reproducible results were obtained.

#### IV. PRESENTATION OF DATA

The phase diagram as presented in Figure 4 for the uranium-zirconium alloy system was based on thermal, microscopic and X-ray data with the exception of certain lines which were drawn from consideration of the phase rule. The portions which are not clearly established by experimental results are indicated by dotted lines. The hardness of the alloys, their working properties and chemical analysis are presented in separate sections. The bomb reduction method of preparing uranium-zirconium alloys is discussed and an attempt made to evaluate its usefulness.

##### A. Thermal Data

The thermal data obtained in this investigation can be most logically discussed in two parts, the data connected with the melting points of the alloys and the data on transition temperatures of the alloys. The melting point data for many of the alloys are tabulated in Table 1 and plotted against composition in Figure 5. They were all determined by the optical pyrometer method as described previously except for the 1.88 and 4.75 per cent zirconium samples. On these two samples a cooling curve was run using a chromel-alumel thermocouple. In this case both the liquidus and solidus temperatures were established. The temperatures observed for these two samples were probably slightly low since these were cooling curves and the rate of cooling was quite fast.

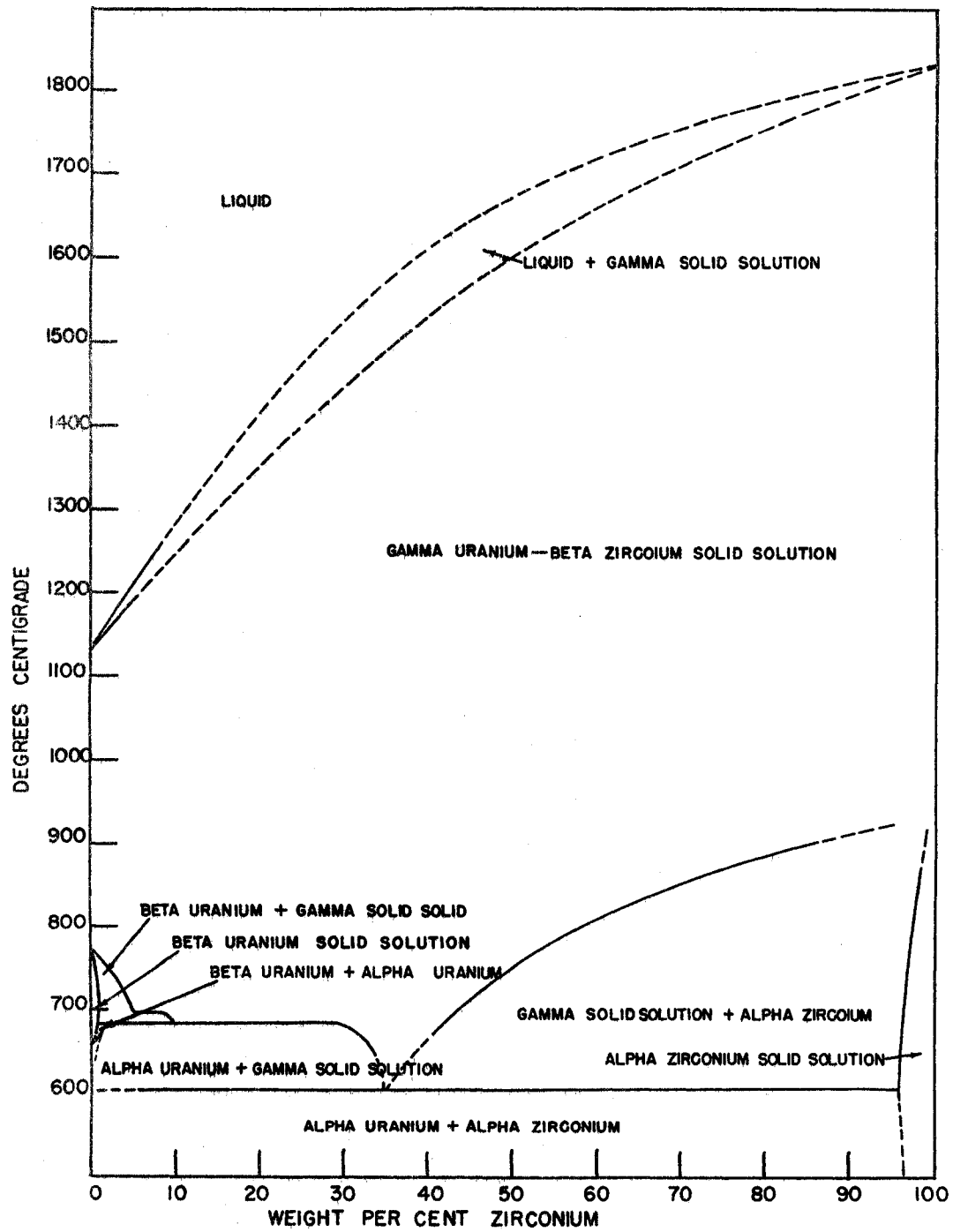


Figure 4 - Phase diagram of uranium-zirconium system.

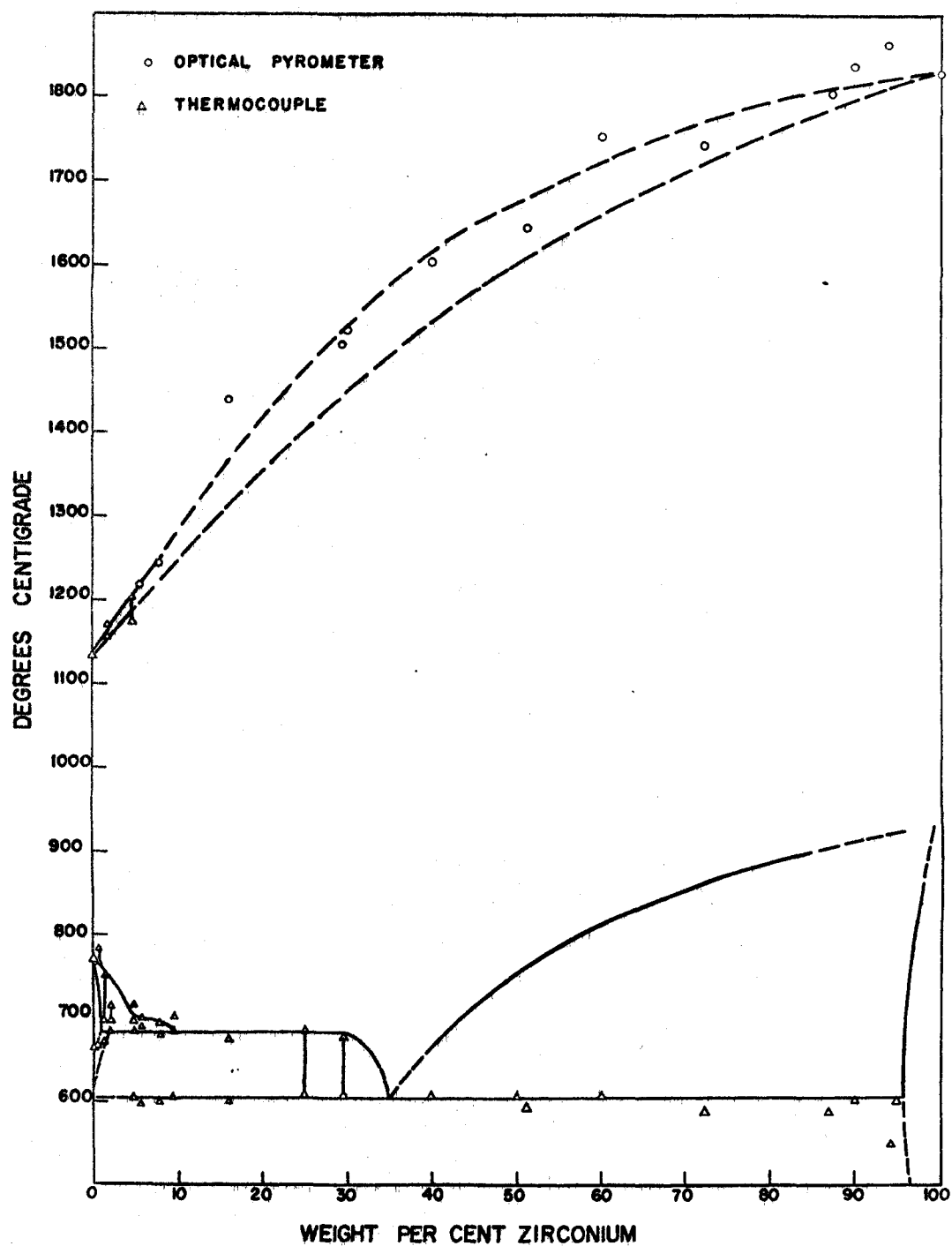


Figure 5 - Thermal data from investigation of uranium-zirconium system.

TABLE 1

Melting Data from Uranium-Zirconium Alloys

Composition		Observed Melting
% Uranium	% Zirconium	Temperature
100		1125
97.11	1.88	1158-1170 <sup>d</sup>
94.30	4.75	1176-1206 <sup>d</sup>
92.63	5.43	1220
89.05	7.90	1245
82.86	15.98	1434
82.86	15.98	1449
69.47	30.10	1526
68.41	29.45	1506
59.50	40.30	1608
46.01	52.24	1648
-----	60	1758
24.53	72.22	1734
24.53	72.22	1754
10.05	87.30	1806
10.05	87.30	1801
-----	90	1840
4.41	94.30	1864
	100 <sup>b</sup>	1780
	100 <sup>a</sup>	1825
	100 <sup>c</sup>	1800

<sup>a</sup> Prepared by bomb reduction in dolomitic oxide liner

<sup>b</sup> Crystal-Bar zirconium

<sup>c</sup> Prepared by bomb reduction in graphite liner

<sup>d</sup> Obtained by thermal analysis using chromel-alumel thermocouple



The melting data obtained by the optical pyrometer method must be between the liquid and solidus temperatures. Since an appreciable amount of liquid is necessary before any liquid would be observed in the cavity and an oxide or nitride surface film would tend to keep the liquid from flowing, the observed points probably are considerably above the solidus temperature. The samples usually were sufficiently liquid at temperatures slightly above the first observed melting to cause rupture of the bar. Microscopic examination of the bars in the region of fusion was made in an effort to determine the relative amounts of liquid and solid which had been present at the fusion point. However, no indication of the relative amounts of liquid and solid phases present at fusion was found. This may have been due to rapid homogenization of the samples as they cooled through the gamma solid solution region. The temperature of the first observed melting was quite sensitive to oxidation of the sample so the data from experiments in which the sample had become visibly oxidized were not used. In most cases melting was observed and the current turned off before the bar fused in two. In these cases a new cavity was drilled in the bar and the melting experiment repeated. The greatest difference between two runs on the same sample was 20° C and the agreement was usually much closer than this. The accuracy of the temperature measurement with this type of apparatus is estimated by Chiotti<sup>35</sup> as  $\pm 25^{\circ}$  C.

The melting data formed a smooth curve when plotted against the composition of the alloys. There was no maximum or minimum in

the curve nor was there any indication of a horizontal portion. This was good supporting evidence for a continuous solid solution between beta zirconium and gamma uranium. The curve extrapolated quite smoothly to the melting point of uranium but considerable scattering was encountered at the zirconium end of the curve. This was caused by the variation of the melting point of zirconium and alloys of zirconium with purity. The melting points as determined in this laboratory for various samples of zirconium prepared by different methods are also given in Table 2. The literature value of  $1830^{\circ} \text{C} \pm 40^{\circ}$  covers all the above observed values but this large variation in observed melting points is no doubt due to variation in purity as well as errors in measuring temperature.

The solid state transitions in this alloy system were studied very intensively by thermal analysis. The thermal effects which were obtained during heating are tabulated in Table 2, and are plotted against the composition of the alloys in Figure 5.

In Table 2, the thermal effects which occurred over a range of temperature were indicated by giving the initial and final temperature and separating them with a dash. On Figure 5 such a temperature range was indicated by a vertical line connecting the initial and final temperature of the break in the heating curve. The thermal data obtained on cooling are also tabulated in Table 2 to show the large differences in temperature obtained by heating and cooling methods and to permit a comparison of these data with data of other investigators who have used only cooling curves.

TABLE 2

Solid State Transition Data from Uranium-Zirconium Alloys

(Alloys prepared in dolomitic oxide liners except where otherwise noted.)

% U	% Zr	Heating arrests °C.		Cooling arrests °C.	
100		687	772	657	770
100 <sup>a</sup>		666	771	648	765
98.71	0.57	668	768-783	649	766
96.15	1.18	671	697-752	633	723
97.11	1.88	683	699-716	607	673
94.30	4.75	605	683	699-716	602
92.63	5.43	599-613	690	692-697	669
89.05	7.90	600-616	680	690-687	662
89.55	7.62	600-607	683	697	593-607
88.35	9.29	607-617	685	702	614
89.15	9.42	607	683	699-704	609
82.86	15.98 <sup>b</sup>	600-614	673		593-610
-----	25	609-623	623-685		602-614
68.41	29.45 <sup>b</sup>	607-614	614-678		586-600
69.47	30.10 <sup>c</sup>	605-619	619-680		607
59.50	40.30 <sup>c</sup>	607-616			607
47.50	51.20 <sup>b</sup>	593-610			580-596
46.01	52.24 <sup>b</sup>	612-623			591-602
50.40	48.95				600
	60	607-614			607
24.53	72.22 <sup>b</sup>	589-603			598
-----	75	605			579
10.05	87.30 <sup>b</sup>	589			591
-----	90 <sup>c</sup>	602-607			
-----	95	602			
4.41	94.30 <sup>b</sup>	547-593			
	100 <sup>d</sup>				865

<sup>a</sup> Mallinkrodt Biscuit Uranium

<sup>b</sup> Alloy prepared by bomb reduction in graphite liner

<sup>c</sup> Alloy prepared by arc melting

<sup>d</sup> Crystal-bar zirconium

The beta to gamma transition in uranium was found to be lowered rapidly by the solubility of zirconium in gamma uranium. The alpha to beta transition, on the other hand, was raised to  $683^{\circ}\text{C}$  at 1.88 per cent zirconium and the two transitions appeared to have merged at this temperature. The thermal arrest at  $683^{\circ}\text{C}$  was quite pronounced and reached a maximum intensity at about 14.57 per cent zirconium. A change in slope of the heating curve above  $683^{\circ}\text{C}$  was observed in the alloys up to 9.42 per cent zirconium. This was due to the transition from beta to gamma uranium, which occurs over a range of temperature in this region.

A thermal arrest at  $605^{\circ}\text{C}$  was observed in all alloys from 4.75 per cent zirconium through 95 per cent zirconium. This thermal arrest reached a maximum magnitude at about 50 per cent zirconium. In 25, 28.65 and 29.45 per cent zirconium samples, a change in slope from the horizontal thermal arrest at about  $605^{\circ}\text{C}$  up to about  $683^{\circ}\text{C}$  was found. This change in slope of the heating curves was greatest at about  $683^{\circ}\text{C}$  where the curve became almost horizontal. No evidence of this thermal arrest at  $683^{\circ}\text{C}$  was detected beyond 30.10 per cent zirconium. In alloys containing more than 40 per cent zirconium, no heat effect above the  $605^{\circ}\text{C}$  transition was observed up to  $900^{\circ}\text{C}$ . If this arrest at  $605^{\circ}\text{C}$  were a eutectoid transition arising from the alpha to beta transition in zirconium, a change in slope of the heating curve above  $605^{\circ}\text{C}$  would have helped locate the limits of the two phase region above the eutectoid. However thermal effects due to sloping phase boundaries in the solid state

are often not detected by thermal analysis curves.

The thermal arrest at  $605^{\circ}\text{C}$  seemed to be caused by a very rapid and readily reversible reaction. The temperature at which it was observed was changed but very slightly when considerable changes were made in the heating or cooling rates. Also, there was only a small difference between the temperatures at which the arrest was observed in heating curves and cooling curves.

The heat affect associated with the alpha-beta transition in zirconium was observed at  $865^{\circ}\text{C}$  in a sample of crystal-bar zirconium. A sample of Bureau of Mines Sponge gave a very weak break on a cooling curve which occurred over a range of temperature. The temperature at which it started could not be detected but the lower temperature limit was  $864^{\circ}\text{C}$ . This arrest was not observed in heating curves on any zirconium except crystal-bar zirconium and was not detected at all in any of the uranium-zirconium alloys. DeBoer<sup>37</sup> has reported that the presence of even small amounts of oxygen and nitrogen in solid solution in zirconium metal raises the alpha-beta transformation temperature and causes it to occur over a range of temperature. This probably is the reason for failure to obtain an invariant point in the thermal analysis curves of zirconium samples. In the uranium-zirconium alloys the solubility of uranium in beta zirconium would also cause the transformation to take place over a temperature range down to  $605^{\circ}\text{C}$  and should make the thermal effect quite difficult to detect.

The solid state thermal effects which were observed for this

alloy system, with the exception of the alpha-beta transition in zirconium, do not seem to be affected materially by the small amount of oxide or carbide ordinarily present in the samples. The high zirconium alloys which were prepared by bomb reduction in dolomitic oxide liners undoubtedly contained a considerable amount of oxide. They were harder and differed in microstructure as compared to alloys prepared by bomb reduction in graphite liners or by arc melting. However, the thermal data were the same for alloys of the same uranium-zirconium ratio prepared by any of the three methods. Several cases were observed in which alloys of the same uranium-zirconium ratio contained quite widely varying amounts of carbon but thermal analysis of these alloys showed no appreciable difference in transition temperatures.

#### B. Microscopic Examination

The nature and extent of the solid phase fields were also studied by microscopic examination of slowly cooled and of quenched samples. In Figure 6 is shown the extent of the various phase fields as indicated by microscopic evidence. Alloys up to 30.10 per cent zirconium slowly cooled from 900° C had a two phase structure consisting essentially of uniformly dispersed lamellae. This structure is quite similar in appearance to pearlite of the iron - carbon system. The exact eutectoid composition could not be deduced from these microstructures since no primary uranium or zirconium could be

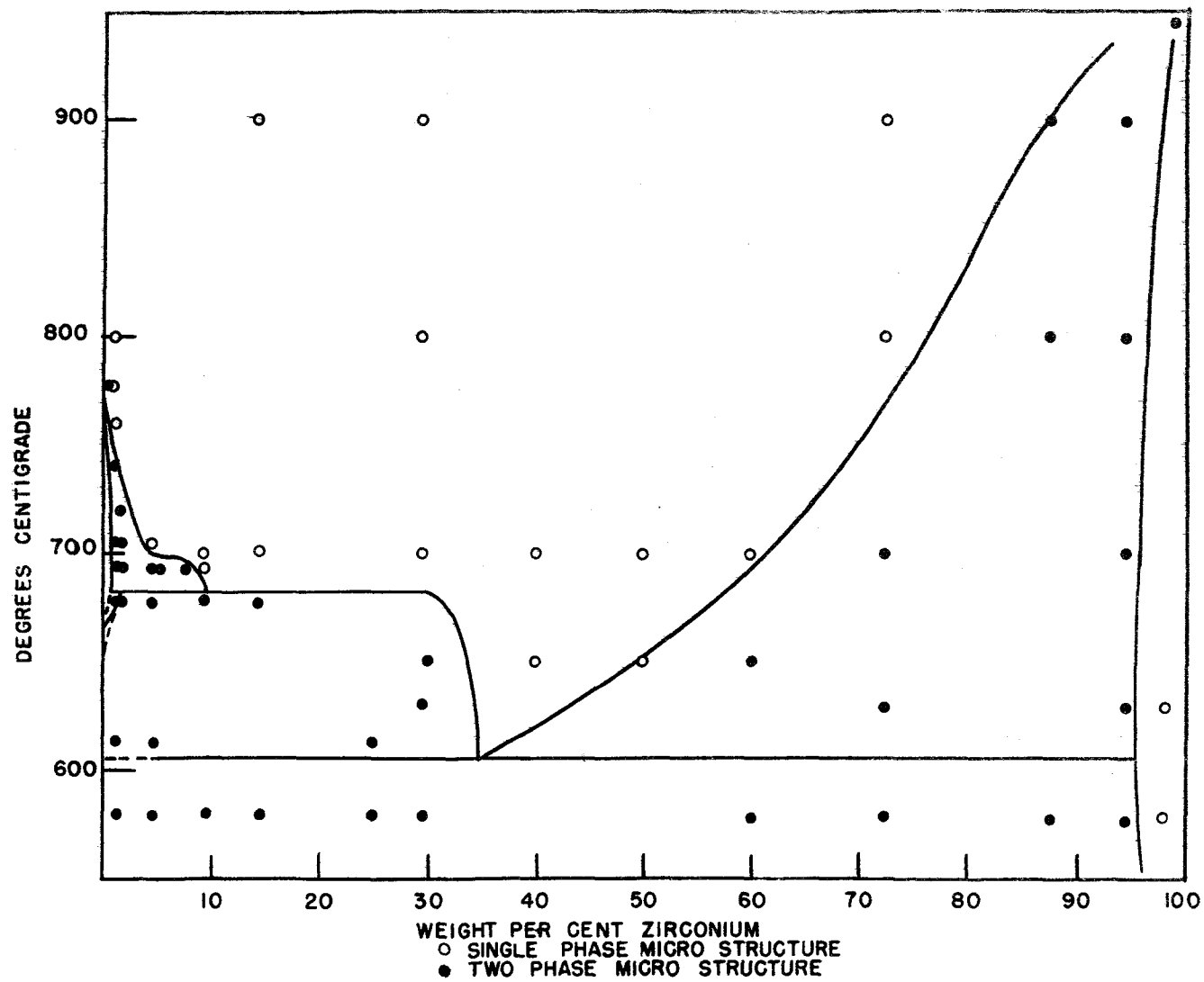
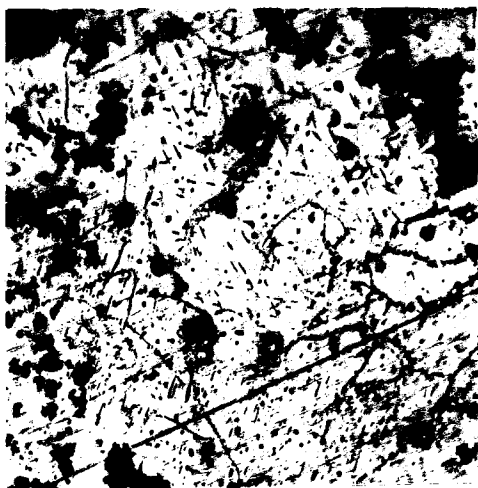


Figure 6 - Microscopic data from uranium-zirconium system.

observed. The reason for failure to observe primary uranium may have been that the alloys were not cooled through the two-phase region above the eutectoid slowly enough for large primary crystals to be formed. The microstructures of these alloys were not changed appreciably by quenching from temperatures below  $683^{\circ}\text{C}$ . A solubility of zirconium in alpha uranium of less than 0.57 per cent was determined by examination of the 0.57 per cent alloy as quenched from  $579^{\circ}\text{C}$ . In Figure 7, which shows this sample, can be seen small particles of zirconium precipitated along the grain boundaries and within the grains. Etching this alloy to reveal the grain boundaries and precipitation was very difficult and only two of the samples of this alloy were prepared for photomicrographs.

The 1.18 per cent alloy is shown in Figure 8 in the slow cooled condition. The microstructure consists of zirconium precipitated in a uranium matrix. This same alloy is shown in Figures 9 and 10 as quenched from  $614^{\circ}\text{C}$  and  $678^{\circ}\text{C}$ . These photomicrographs show that little or no change in the relative amounts of the phases had taken place. A similar series of pictures is shown for the 1.88 per cent alloy in Figures 11, 12 and 13. In Figure 11 may be seen the outlines of prior grains which have undergone a eutectoid precipitation. Since the grain boundary phase appears to be uranium, this would indicate that this was a hypo-eutectoid alloy. The 4.75 per cent alloy, shown in Figures 14 and 15 has an outline of uranium around the prior grains and also appears to have been a hypo-eutectoid alloy. The amount of zirconium precipitated in these alloys increases as the

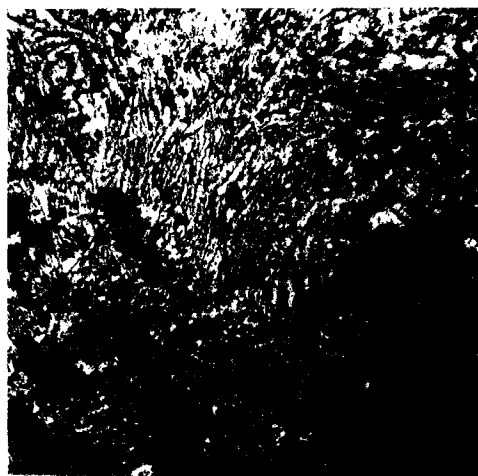




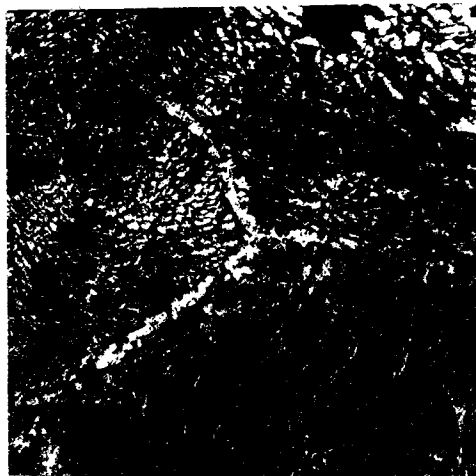
7



8



9



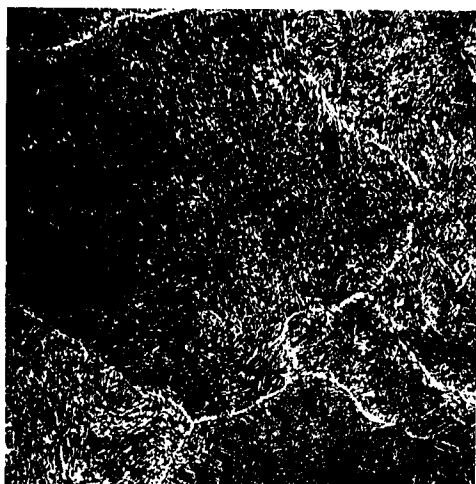
10

Figure 7 - 0.57% zirconium. Quenched from 579° C. Zirconium precipitated in alpha uranium. 10% citric acid elec. etch. X 250.

Figure 8 - 1.18% zirconium. Slow-cooled. Zirconium in uranium. Phosphoric acid elec. etch. X 150.

Figure 9 - 1.18% zirconium. Quenched from 614° C. Same as above. 5% citric elec. etch. X 250.

Figure 10 - 1.18% zirconium. Quenched from 678° C. Same as above. 5% citric elec. etch. X 250.



11



12



13



14

Figure 11 - 1.88% zirconium. Quenched from 579° C. Zirconium lamellae in uranium. X 150.

Figure 12 - 1.88% zirconium. Quenched from 657° C. Same as above. X 150.

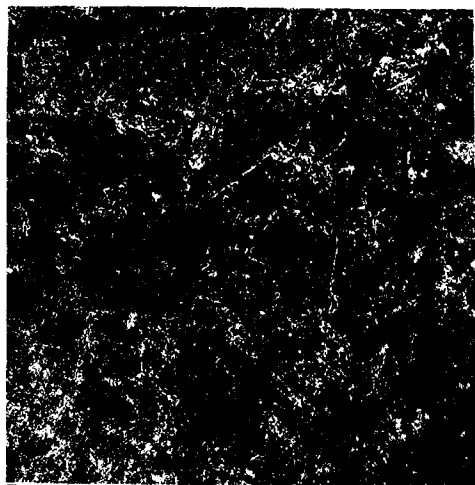
Figure 13 - 1.88% zirconium. Quenched from 678° C. Same as above. X 250.

Figure 14 - 4.75% zirconium. Quenched from 579° C. Same as above. X 500.

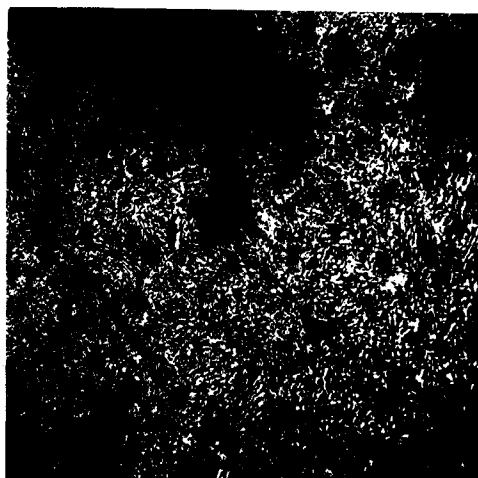
Above samples phosphoric acid elec. etch.

zirconium content increases and alloys containing more than 5 per cent zirconium have such a finely dispersed eutectoid structure that it is almost impossible to resolve under the microscope. The 9.42 per cent alloy quenched from  $678^{\circ}\text{C}$  which is shown in Figure 16, has a eutectoid structure with no indication of prior grains. As the phase diagram is drawn, this alloy underwent a eutectoid decomposition at  $683^{\circ}\text{C}$  directly from a one phase region and there should be no evidence of a primary phase in the structure. That this same phase region extends beyond 30.10 per cent is indicated by pictures of the 25 and 30.10 per cent alloys which are Figures 17 and 18. The clear areas present in the 25 per cent alloys were probably oxide inclusions. This alloy was made by bomb reduction in a dolomitic oxide liner. The 30.10 per cent alloy which does not show these large clear areas was made by arc melting and should have been relatively free of oxygen. No alloys containing more than 30.10 per cent zirconium had this eutectoid microstructure.

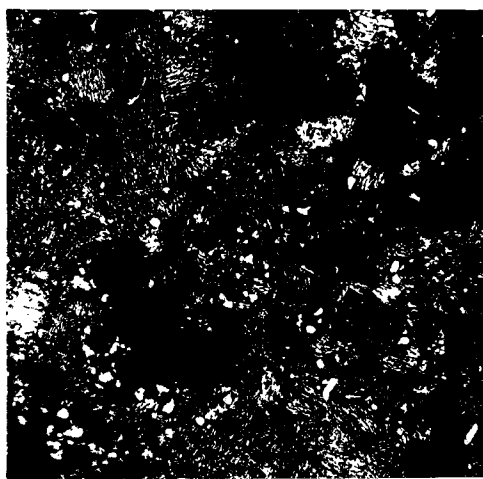
A two phase region was found above the  $683^{\circ}\text{C}$  eutectoid temperature in a composition range from below 1.18 per cent to above 7.90 per cent zirconium. The upper temperature boundary limits of this region are of peculiar shape and represent the lowering of the beta-gamma transition. The horizontal section of this boundary at  $697^{\circ}\text{C}$  shown between about 5 per cent and 8 per cent zirconium seems to extend into the region of less than 5 per cent zirconium. In fact, thermal arrests at this temperature have been observed in samples containing as little as 1.18 per cent zirconium. This line



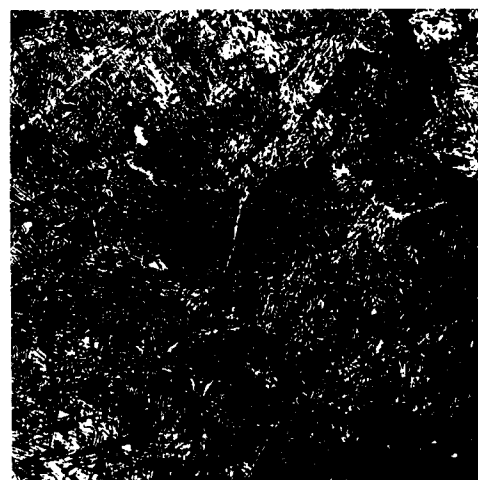
15



16



17



18

Figure 15 - 4.75% zirconium. Quenched from 678° C. Zirconium lamellae in uranium. Phosphoric acid elec. etch.

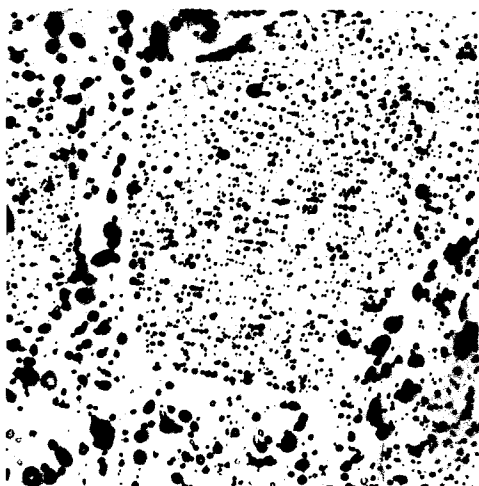
Figure 16 - 9.42% zirconium. Quenched from 678° C. Same as above. 5% HF in Methyl Alc. etch.

Figure 17 - 25% zirconium. Quenched from 614° C. Same as above. Nitric acid base etch.

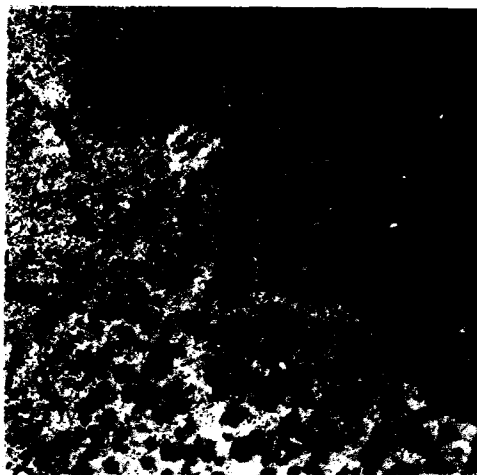
Figure 18 - 30.10% zirconium. Quenched from 650° C. Same as above. Nitric acid base etch.

extension, which is dotted in the diagram, divides the two phase, beta and gamma solid solution, area into two parts. No satisfactory explanation has been obtained from thermal or quenching data for this division. There might be the possibility that the gamma solid solution undergoes order-disorder arrangements above and below this line.

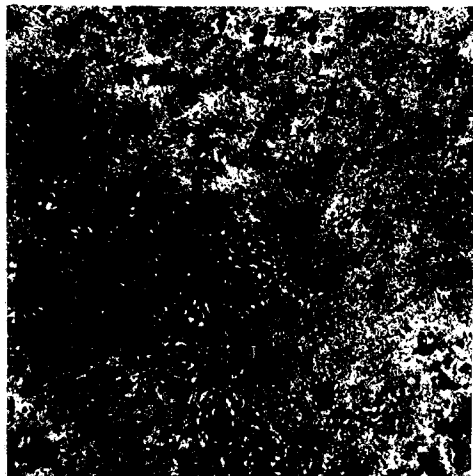
A series of alloys from 1.18 to 9.42 per cent zirconium was heated to  $694^{\circ}\text{C}$  and quenched. The photomicrographs of their structures are shown in Figures 19, 20, 21, 22, 23, 24, 25 and 26. The 1.18 and 1.88 per cent alloys had such a finely dispersed second phase that it was necessary to use 1000 magnification. As a result of this fine dispersion and high magnification, the discontinuous phase appeared black in these two alloys but was light in the alloys containing more zirconium. This light phase is the gamma solid solution and an increase in the amount of this phase was observed with increasing zirconium content. The 9.29 and 9.42 per cent alloys contained only this phase. At  $705^{\circ}\text{C}$ , the two phase region extends only up to about 4.0 per cent. This was established by quenching the 1.18, 1.88, 4.75 and 7.62 per cent alloys from that temperature. The microstructures of these samples are shown in Figures 27, 28, 29 and 30. The 4.75 and 7.62 per cent alloys contained only a single phase and the ratio of the two phases in the 1.88 per cent alloy had changed noticeably. By application of the lever arm relation, the gamma solubility limit at this temperature would be in the neighborhood of 3.50 per cent zirconium. The 1.88



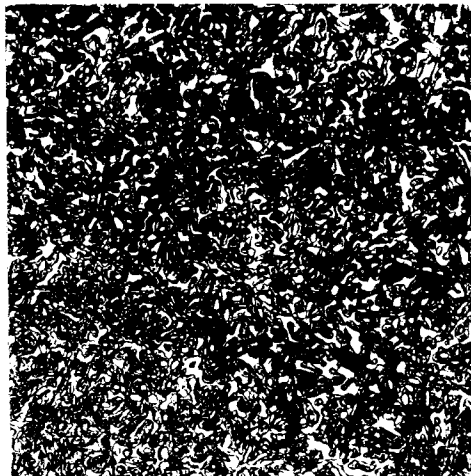
19



20



21



22

Figure 19 - 1.18% zirconium. Beta plus gamma solid solution (dark areas). Phosphoric acid elec. etch. X 1000.

Figure 20 - 1.88% zirconium. Same as above. Nitric acid base etch. X 1000.

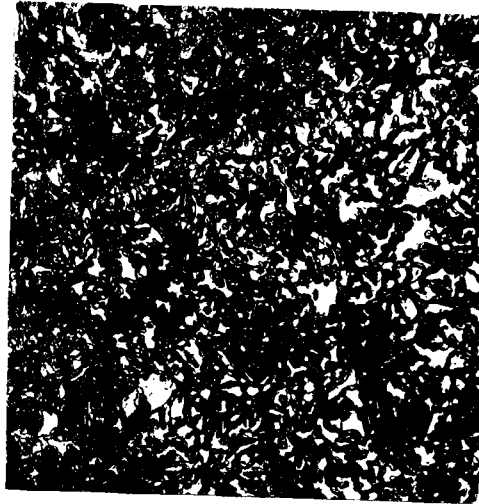
Figure 21 - 4.75% zirconium. Beta plus gamma solid solution (lighter areas). Nitric acid base etch. X 250.

Figure 22 - 5.43% zirconium. Same as above. Nitric acid base etch. X 250.

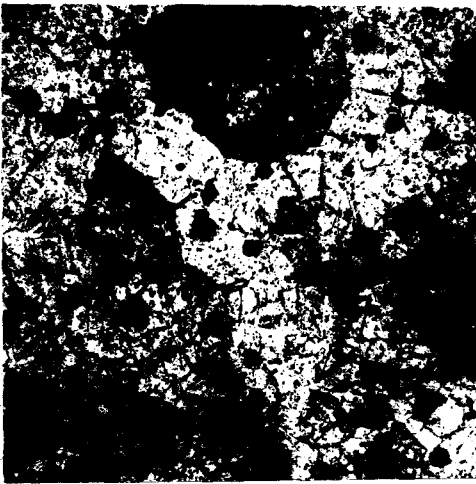
Above alloys quenched from 694° C.



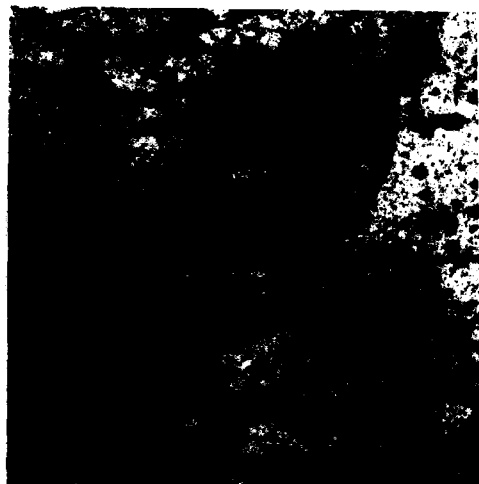
23



24



25



26

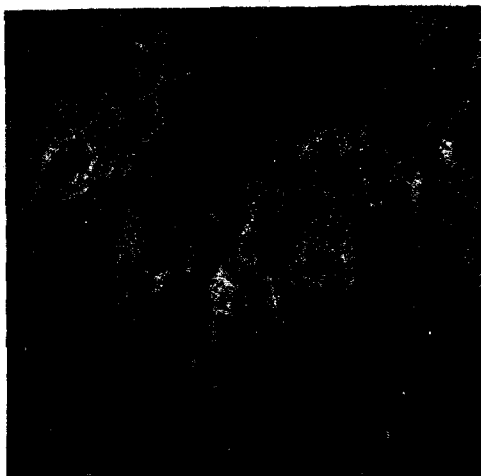
Figure 23 - 7.62% zirconium. Beta uranium plus gamma light areas of solid solution.

Figure 24 - 7.90% zirconium. Same as above.

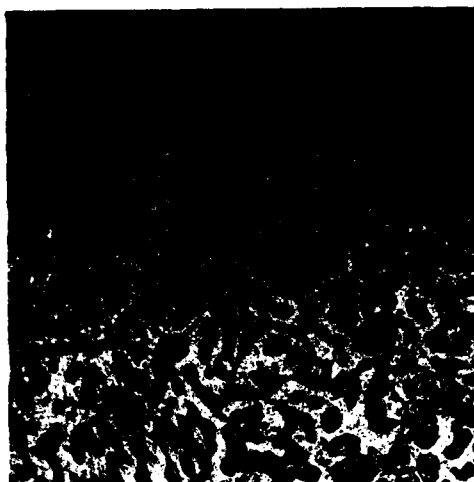
Figure 25 - 9.29% zirconium. One phase, gamma solid solution.

Figure 26 - 9.42% zirconium. One phase, gamma solid solution.

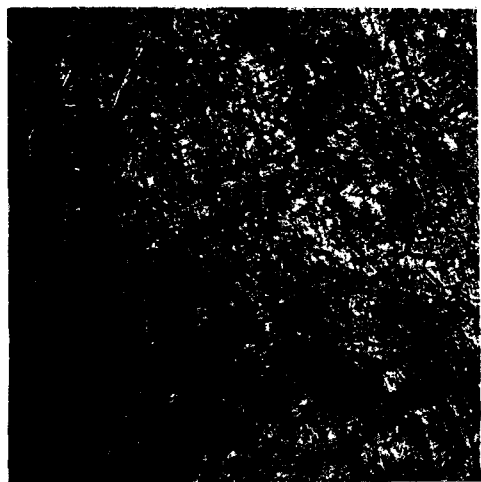
Above samples quenched from 694° C. Nitric acid base etch. X 250.



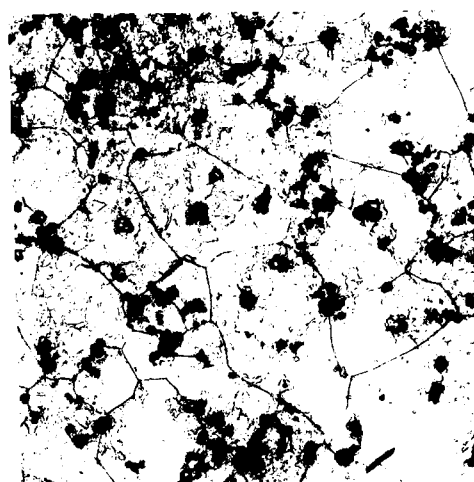
27



28



29



30

Figure 27 - 1.18% zirconium. Beta uranium plus gamma solid solution. X 500.

Figure 28 - 1.88% zirconium. Same as above. X 250.

Figure 29 - 4.75% zirconium. One phase, gamma solid solution. X 250.

Figure 30 - 7.62% zirconium. One phase, gamma solid solution. X 250.

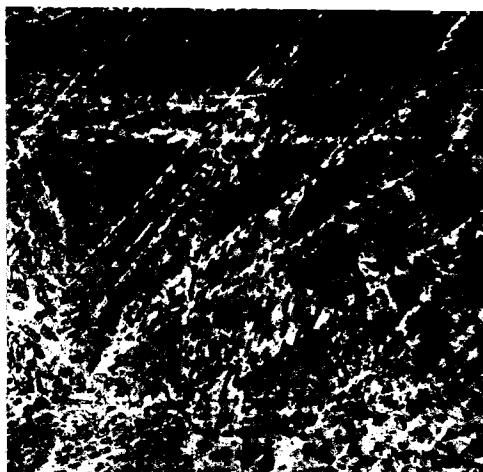
Above samples quenched from 705° C. Phosphoric acid elec. etch.



and 1.18 per cent alloys quenched from 720° C still consist of two phases, as shown in Figures 31 and 32. Quenched from 740° C, the 1.18 per cent alloy as seen in Figure 33 was still in the two phase region. The sample of the 0.57 per cent alloy was quenched from 778° C. This alloy as shown in Figure 34 consists of approximately equal amounts of two phases which must be beta uranium and gamma solid solution. It is evident that the gamma-beta solid solution stable at 778° C decomposed during the quench.

A two-phase field was also found above the 605° C horizontal for zirconium-rich alloys. In this region alpha zirconium solid solutions precipitate from the gamma-beta solid solutions on cooling over a range of temperature. A series of photomicrographs of alloys quenched from within this field is shown in Figures 35 through 46. The needles, which usually appear dark, are alpha zirconium solid solution and the clear, light matrix is gamma-beta solid solution. The ratio of alpha zirconium to gamma-beta solid solution increases with increasing zirconium content and with decreasing quenching temperature.

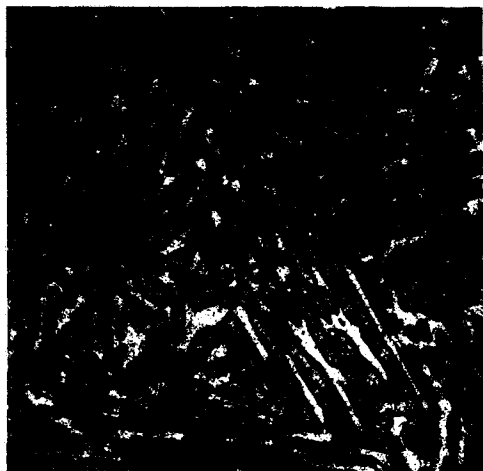
The alpha to beta transformation in pure zirconium has been reported to take place at 863° C in metal produced by the iodide hot wire process. DeBoer and Fast<sup>30</sup> have reported that oxygen or nitrogen dissolved in zirconium raises the transformation temperature and causes it to take place over a range of temperature. They have postulated that a two phase region should exist in the oxygen-zirconium phase system corresponding to the temperature range over which



31



32



33



34

Figure 31 - 1.18% zirconium. Quenched from  $720^{\circ}$  C. Beta uranium plus gamma solid solution.

Figure 32 - 1.88% zirconium. Quenched from  $720^{\circ}$  C. Same as above.

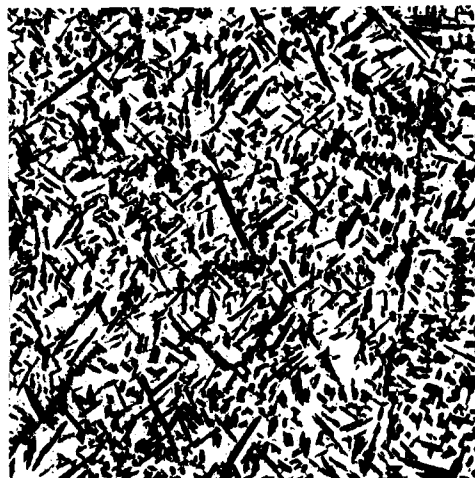
Figure 33 - 1.18% zirconium. Quenched from  $740^{\circ}$  C. Same as above.

Figure 34 - 0.57% zirconium. Quenched from  $778^{\circ}$  C. Same as above.

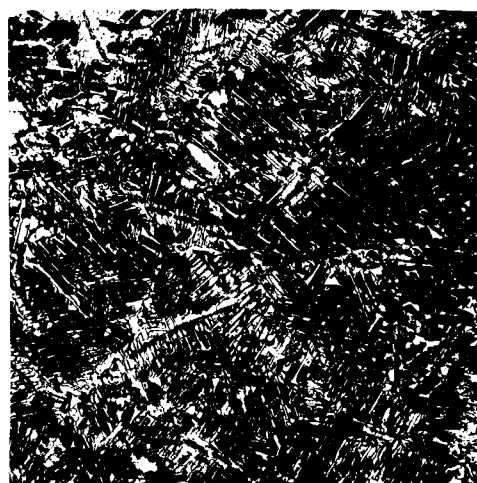
Above samples etched with nitric acid base etch except Figure 34 which was 10% oxalic acid elec. etch. X 250.



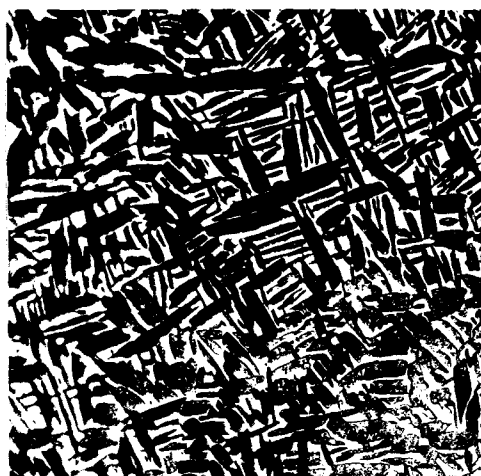
35



36



37



38

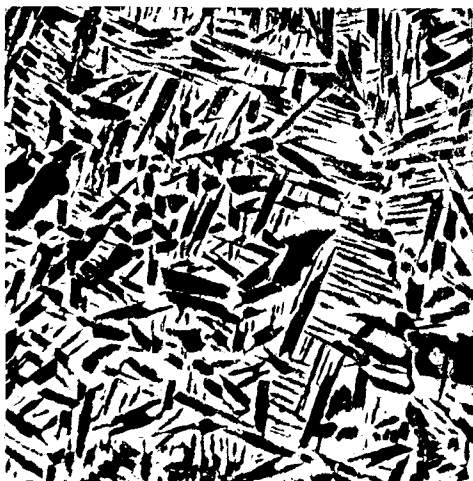
Figure 35 - 72.22% zirconium. Quenched from 630° C. Alpha zirconium needles plus gamma-beta solid solution.

Figure 36 - 72.22% zirconium. Quenched from 700° C. Same as above.

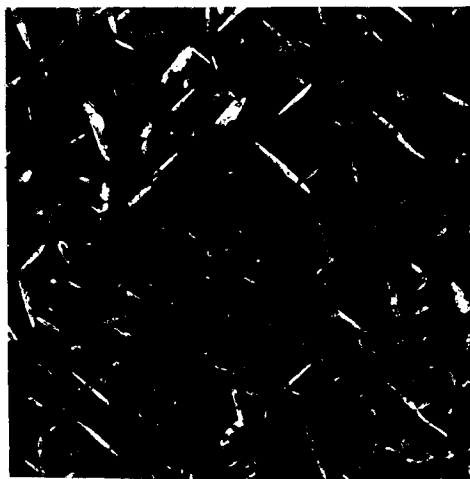
Figure 37 - 87.30% zirconium. Quenched from 630° C. Same as above.

Figure 38 - 87.30% zirconium. Quenched from 700° C. Same as above. Note decrease in needle phase.

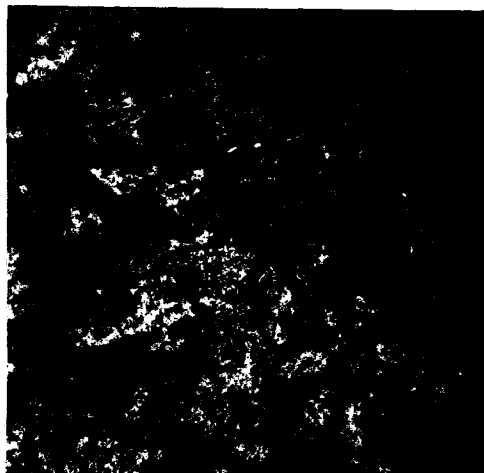
Above samples etched with nitric acid base etch. X 250.



39



40



41



42

Figure 39 - 87.30% zirconium. Quenched from 800° C. Alpha zirconium needles plus gamma beta solid solution.

Figure 40 - 87.30% zirconium. Quenched from 900° C. Same as above. Alpha zirconium is the light phase.

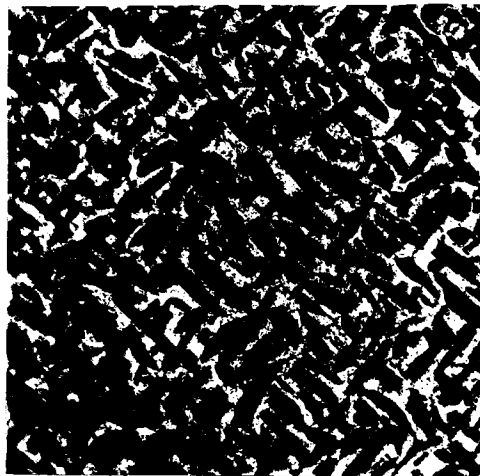
Figure 41 - 94.30% zirconium. Quenched from 630° C. Same as above. Very little gamma-beta solid solution.

Figure 42 - 94.30% zirconium. Quenched from 700° C. Same as above.

Above alloys etched with nitric acid base etch. X 250.



43



44



45



46

Figure 43 - 94.30% zirconium. Quenched from 800° C. Dark alpha zirconium needles in gamma-beta solid solution.

Figure 44 - 94.30% zirconium. Quenched from 900° C. Same as above

Figure 45 - 94.30% zirconium. Quenched from 900° C. Same as above except alpha zirconium needles are light.

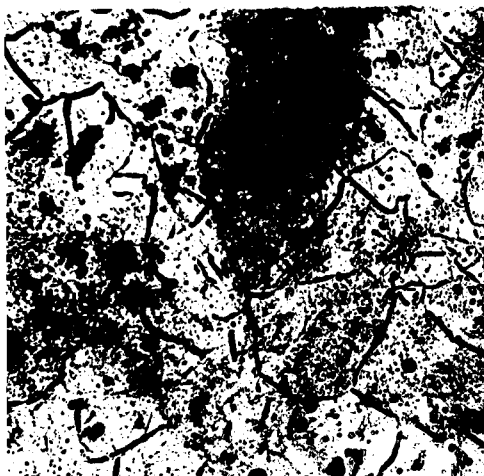
Figure 46 - 97.20% zirconium. Quenched from 930° C. Same as above.

Above alloys etched with nitric acid base etch. X 250.

the transformation takes place. High zirconium uranium alloys heated above  $863^{\circ}\text{C}$  should have been in the gamma-beta solid solution field, but the 87.30 and 94.30 per cent zirconium alloys quenched from  $900^{\circ}\text{C}$  still consisted of two phases. It was necessary to heat to  $1000^{\circ}\text{C}$  to transform these alloys completely to gamma-beta solid solution. The 98 per cent zirconium alloy was definitely in the alpha zirconium plus gamma-beta solid solution region when quenched from  $930^{\circ}\text{C}$ . The presence of oxygen in these alloys must have raised the transition temperature above  $930^{\circ}\text{C}$ .

The alloys quenched from this two phase region would usually react with the etching solution so that the needles were dark and the matrix light in color. However, the same etching solution acting on the same sample would occasionally result in producing reversed contrast. That is, the needles would be light and the matrix would be darker. These alloys were all etched so as to show the needles dark for the sake of uniformity and ease of interpretation of the microstructures. The 94.30 per cent alloy quenched from  $900^{\circ}\text{C}$  is shown in Figure 44 etched to correspond to the other samples shown for this region. Figure 45 is a photomicrograph of the same alloy etched to show light needles on a darker matrix. In both cases the same etching solution was used but the dark needles on a light background were produced by a longer etching time.

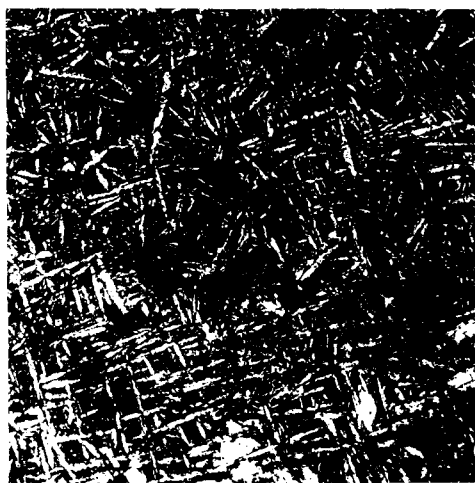
Above all solid two phase regions in the diagram, a continuous solid solubility of beta zirconium and gamma uranium was observed up to the solidus line. The photomicrographs shown in Figures 47 through 62



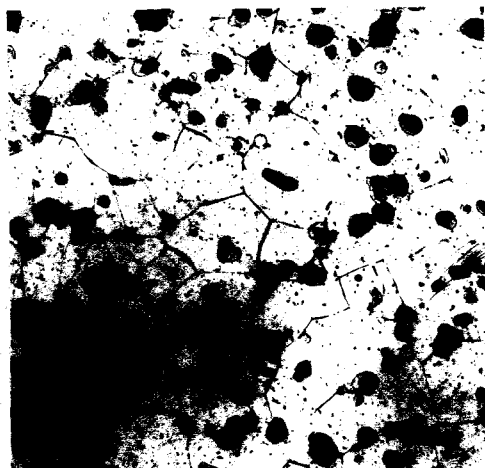
47



48



49



50

Figure 47 - 1.18% zirconium. Quenched from 778° C. 5% citric acid elec. etch. X 150.

Figure 48 - 1.32% zirconium. Quenched from 800° C. 10% citric acid elec. etch. X 150.

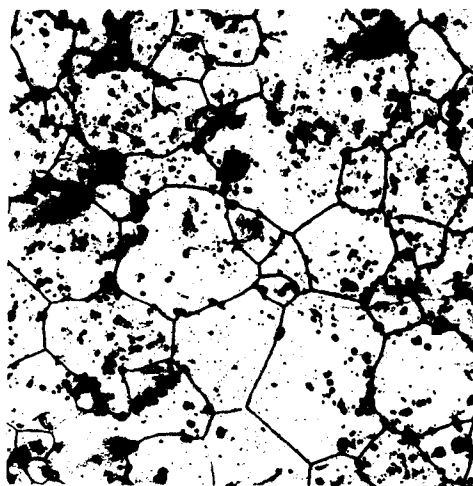
Figure 49 - 1.88% zirconium. Quenched from 778° C. 10% citric acid elec. etch. X 150

Figure 50 - 15.98% zirconium. Quenched from 702° C. Nitric acid base etch. X 250.

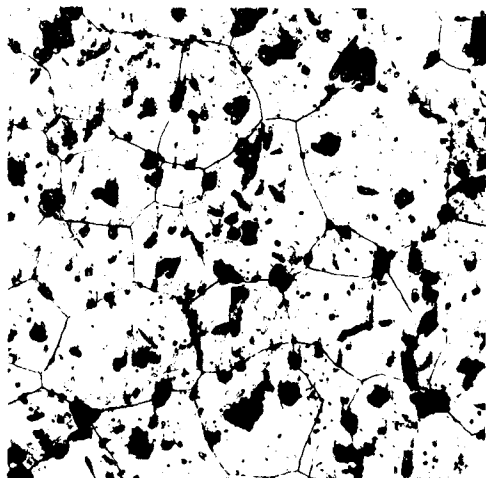
Above alloys are one phase.



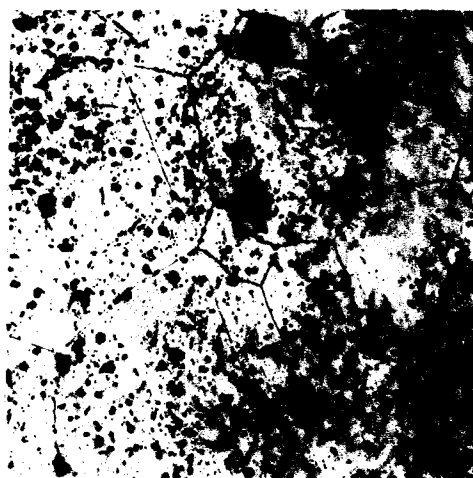
51



52



53



54

Figure 51 - 15.98% zirconium. Quenched from 900° C.

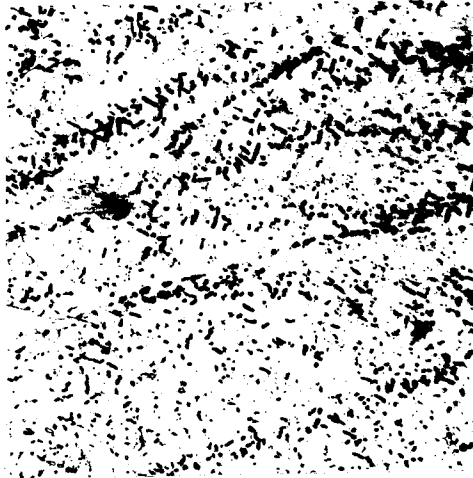
Figure 52 - 25% zirconium. Quenched from 700° C.

Figure 53 - 29.45% zirconium. Quenched from 900° C.

Figure 54 - 30.10% zirconium. Quenched from 700° C.

Above alloys show one phase. Etched with nitric acid  
base etch. X 250.





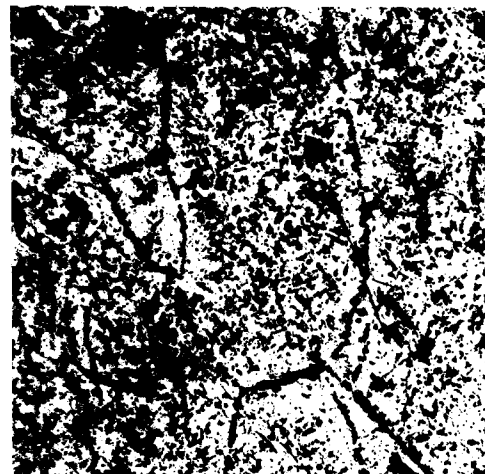
55



56



57



58

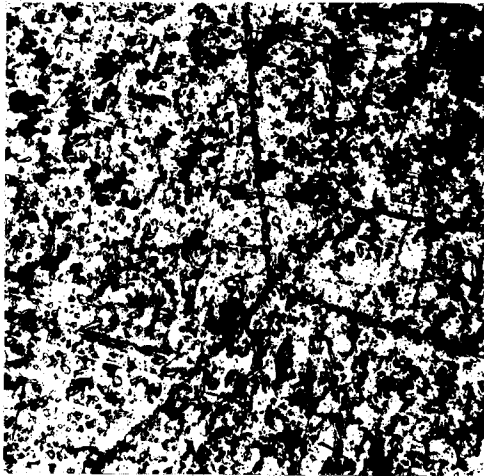
Figure 55 - 40.30% zirconium. Quenched from 650° C.

Figure 56 - 48.95% zirconium. Quenched from 650° C.

Figure 57 - 40.30% zirconium. Quenched from 700° C.

Figure 58 - 48.95% zirconium. Quenched from 700° C.

Above alloys show one phase structure. Nitric acid  
base etch. X 250.



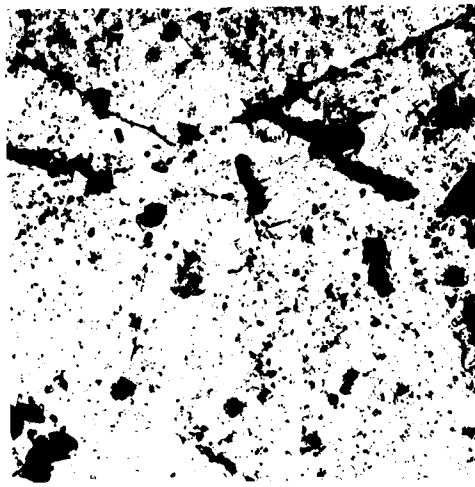
59



60



61



62

Figure 59 - 60% zirconium. Quenched from 700° C.

Figure 60 - 72.22% zirconium. Quenched from 900° C.

Figure 61 - 87.30% zirconium. Quenched from 1000° C.

Figure 62 - 94.30% zirconium. Quenched from 1000° C.

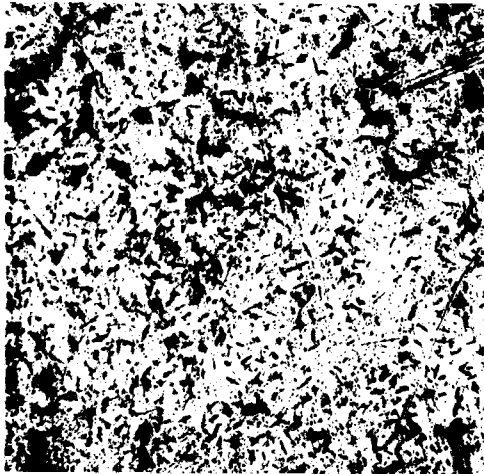
Above alloys show one phase structure. Nitric acid  
base etch. X 250.

lend evidence of this extensive solid solution. The 1.88 per cent alloy quenched from 778° C has a microstructure somewhat similar to martensitic steel and appears to have been quenched from a single phase region but to have undergone some transformation in spite of being quenched. The 1.32 per cent alloy quenched from 800° C has a similar structure and in several other uranium-rich alloys similarly treated some evidence of this structure was observed but it was less conspicuous. The quenched 15.98 and 25.45 per cent alloys have a considerable amount of oxide and carbide inclusions evident in the microstructure which is otherwise one phase.

The alloys from 29.45 through 60 per cent contained a large amount of foreign material in the microstructure. The nitrogen and carbon analyses of these samples did not indicate that they were more impure than alloys of higher and lower zirconium content which appeared much cleaner. A possible explanation is the variation in the amount of oxygen in the samples. Uranium dissolves very little oxygen even at high temperatures but zirconium dissolves oxygen quite readily and holds it in solid solution. Alloys of these two metals might be expected to exhibit an intermediate behavior. Hence, in the low zirconium alloys, the oxygen would never enter into solution and in the high zirconium alloys it would remain in solution. In general, the solubility of oxygen in metals increases with an increase in temperature. Thus, in the intermediate alloys it would be quite reasonable to expect that oxygen would be dissolved at elevated temperatures and precipitated at lower temperatures. The arc-melted samples shown in

Figures 63 and 64 in the as-cast condition had a small amount of precipitation within the grains. The rate of cooling of these alloys from the melting point was fairly rapid since they were in contact with a water cooled copper surface. However, the rate of cooling was not as fast as the water quench which was used after heat-treating the samples. The arc-melted samples shown in Figures 54 through 59 after being heated and quenched have as much or more of this precipitation. Heating the same alloys to  $800^{\circ}\text{C}$  and quenching did not change the appearance of the microstructure. The relative amounts of the needles in this series of alloys was quite constant which indicated that they were not related to the major components of the system. The amount of this phase present in the alloys did vary with the method of preparation of the alloy. In some of the early alloys as shown in Figures 65 and 66 so much of this phase was present that it was mistaken for crystals of primary zirconium or an intermetallic compound. However, as alloys lower in oxygen content were prepared, the amount of this phase decreased but it always made interpretation of the microstructures of the intermediate uranium-zirconium alloys difficult and uncertain. A photomicrograph of a 50 per cent alloy prepared by melting uranium with Bureau of Mines sponge zirconium in a graphite crucible is shown in Figure 67. Carbide areas can be seen in the matrix and have a different appearance than oxide phase.

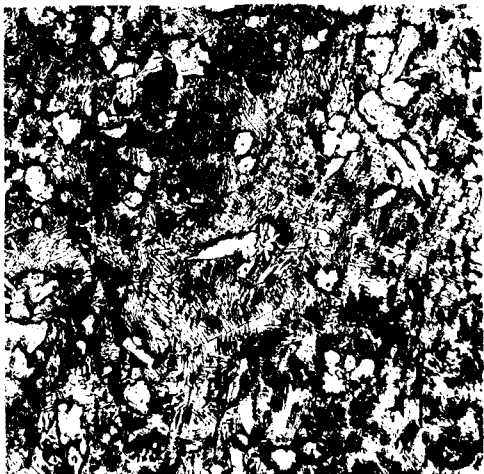
A considerable amount of thermal, microscopic and X-ray evidence indicated that the  $605^{\circ}\text{C}$  horizontal was due to a eutectoid transfor-



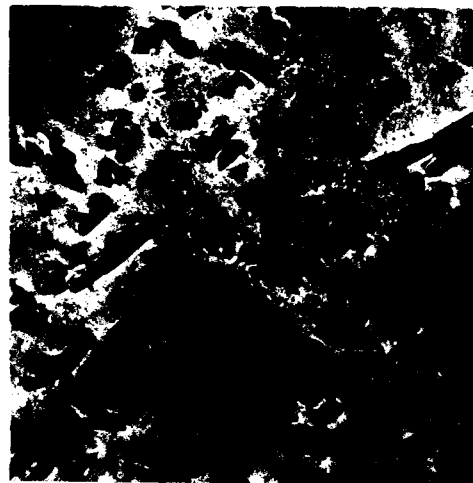
63



64



65



66

Figure 63 - 30.10% zirconium. As-cast. Oxide precipitation. Nitric acid base etch.

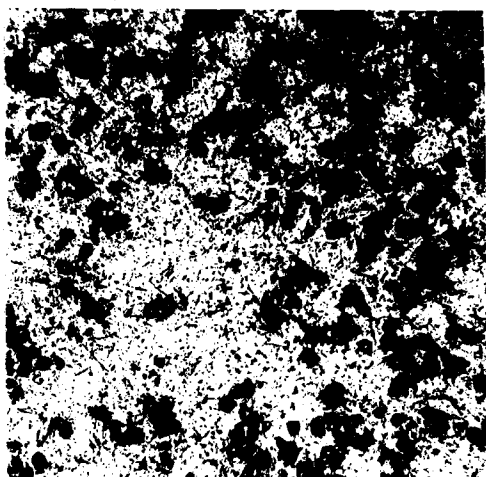
Figure 64 - 48.95% zirconium. As-cast. Same as above. Nitric acid base etch.

Figure 65 - 29.45% zirconium. Quenched from 630° C. Note clear oxide areas. Nitric acid base etch.

Figure 66 - 47.40% zirconium. Slow-cooled. Note large oxide areas. 10% oxalic elec. etch.

mation. However, no normal eutectoid microstructure other than that previously found to be associated with the  $683^{\circ}\text{C}$  transition could be produced in any of the uranium-zirconium alloys. The samples were examined both as-cast and after quenching from temperatures below the  $605^{\circ}\text{C}$  horizontal. Many different etchants and etching procedures were tried but in no case could a clearly defined two phase area with a structure of eutectoid characteristics be found in alloys containing more than 30.10 per cent zirconium. This might have been due to the eutectoid precipitation being so finely dispersed that it could not be resolved by the optical microscope or it might have been due to failure of the etching procedure in revealing the true microstructure. In Figures 68 through 72 are shown typical microstructures from this region. Primary zirconium crystals may be observed in the 48.95, 60 and 72.22 per cent zirconium alloys. The matrix, which according to the diagram should show the eutectoid structure, appears quite clear and no evidence of precipitation could be seen.

The solubility of uranium in alpha zirconium may be estimated from the microstructures of the 4.41 and 2.32 per cent uranium alloys. These alloys as quenched from  $580^{\circ}\text{C}$  are shown in Figures 73 and 74. The 4.41 per cent uranium alloy has a small amount of a second structure between the grains of alpha zirconium. The 2.32 per cent uranium alloy appears to consist only of alpha zirconium solid solution. The 10.05 per cent uranium sample shown in Figure 72 contained much more of the second structure than the 4.41 per cent alloy. These alloys



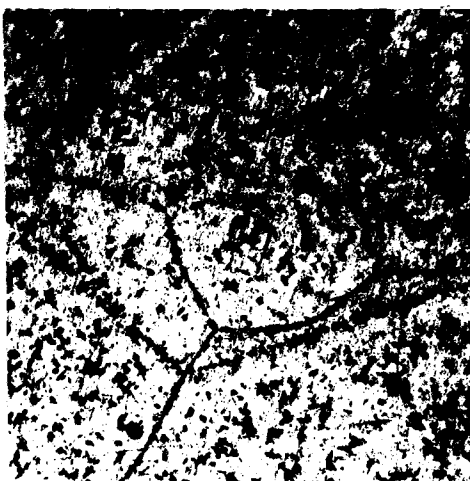
67



68



69



70

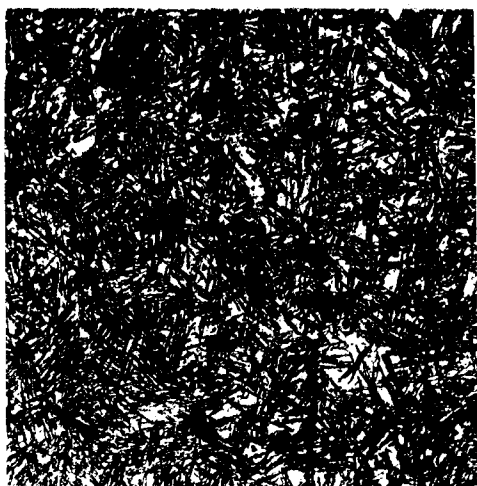
Figure 67 - 50% zirconium. Melted in graphite and slow-cooled.  
Note carbide areas.

Figure 68 - 40.30% zirconium. Quenched from 550° C.

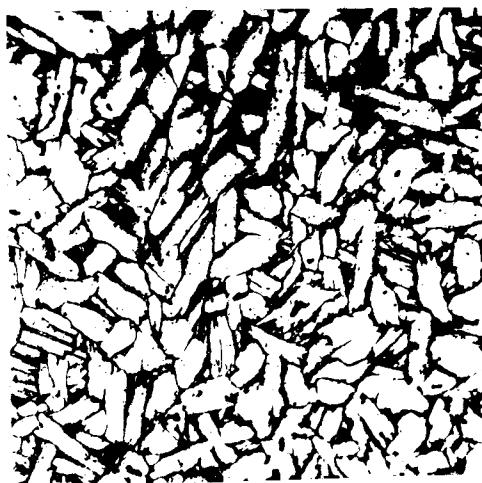
Figure 69 - 48.95% zirconium. Quenched from 550° C.

Figure 70 - 60% zirconium. Quenched from 550° C.

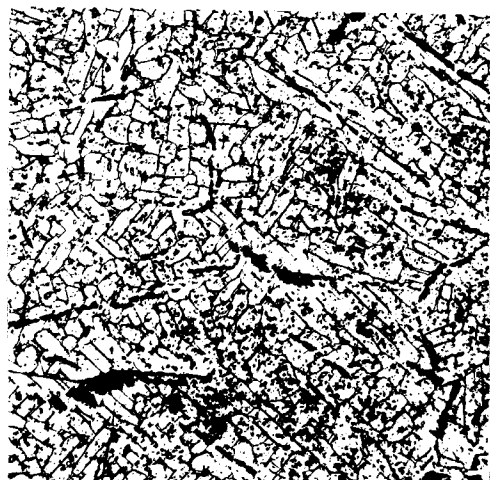
Above samples etched with nitric acid base etch. X 250.



71



72



73



74

Figure 71 - 72.22% zirconium. Light alpha zirconium needles plus second phase, possibly eutectoid.

Figure 72 - 87.30% zirconium. 10.05% uranium. Same as above.

Figure 73 - 94.30% zirconium 4.41% uranium. Alpha zirconium solid solution with small amount of second phase.

Figure 74 - 2.32% uranium. Alpha zirconium solid solution.

Above alloys quenched from 578° C. Nitric acid base etch except Figure 74 which was 10% HF in water. X 250.

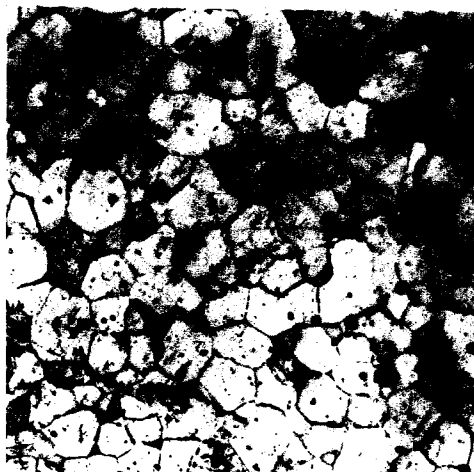


cooled slowly to room temperature showed little change in microstructure so the solubility limit at room temperature must have been about the same as it is at  $580^{\circ}\text{C}$ . The microscopic evidence for this solubility limit is supported by the observation of a thermal arrest at  $605^{\circ}\text{C}$  in the 4.41 per cent uranium alloy and the failure to observe an arrest in the 2.31 per cent alloy.

The microstructure of a sample of zirconium produced by bomb reduction in a graphite liner is shown in Figures 75 and 76. The hardness of this zirconium was Rockwell A-45 in the as-reduced condition. A sample was cold-rolled to 50 per cent reduction in thickness before excessive cracking developed. Figure 75 is a photomicrograph of a sample of the biscuit heated to  $900^{\circ}\text{C}$  and quenched. A sample of the same biscuit after being cold-rolled and then heated to  $900^{\circ}\text{C}$  and quenched is shown in Figure 76. The microstructure of a sample of zirconium produced by bomb reduction in a dolomitic oxide liner is shown in Figure 77 in the as-reduced condition. Figures 78 and 79 show the microstructures of Bureau of Mines cast ingot zirconium as received and as quenched from  $900^{\circ}\text{C}$ . This metal was received by this laboratory during 1948 and probably is inferior to later production. Crystal bar zirconium also received during 1948 is shown in Figure 80 as it was received and in Figure 81 as quenched from  $900^{\circ}\text{C}$ . The microstructures shown in Figures 75 through 81 indicate marked differences that are associated with methods of production and heat treatments of otherwise relatively pure zirconium.



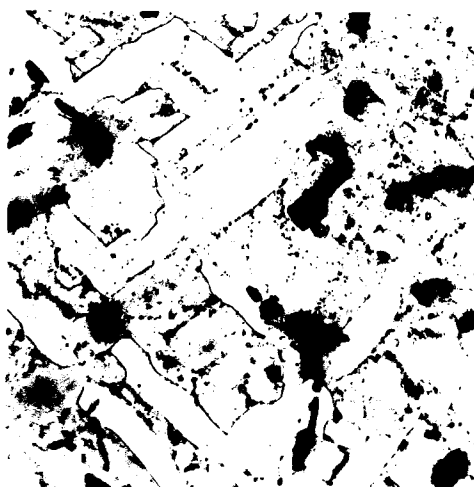
75



76



77



78

Figure 75 - Zirconium. Reduced in graphite. Quenched from 900° C.

Figure 76 - Zirconium. Reduced in graphite. Cold-worked and quenched from 900° C.

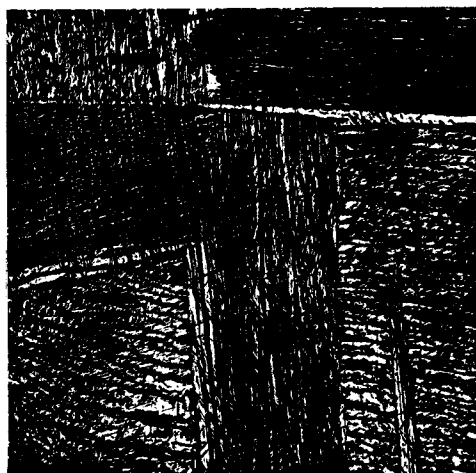
Figure 77 - Zirconium. Reduced in dolomitic oxide. As-reduced.

Figure 78 - Zirconium. Bureau of Mines cast ingot, as received.

Above samples etched by nitric acid base etch. X 250.



79



80



81

Figure 79 - Zirconium. Bureau of Mines cast ingot quenched from 900° C.

Figure 80 - Zirconium. Crystal bar, as received.

Figure 81 - Zirconium. Crystal bar quenched from 900° C.

Above alloys etched with 10% HF in water. X 250.

The examination of diffusion bands in samples in which composition gradients were known to exist was of little aid in studying this system. The bands which were observed could not be correctly interpreted until much of the phase diagram was known from other information. A diffusion sample was prepared by heating a small block of Bureau of Mines ingot zirconium containing a 3/8 inch hole into which a plug of uranium had been driven. The sample was heated to 1200° C under vacuum and held at this temperature for 15 minutes. The uranium had melted and wet the zirconium with some subsequent loss of uranium by creeping over the top of the zirconium block. A section of the sample showing the interface between the part that had melted and the zirconium is shown in Figure 82. At this temperature the liquid should have contained about 8 per cent zirconium if the equilibrium state had been reached. The small amount of zirconium precipitated in the main body of the liquid indicated that probably less than two per cent zirconium had gone into solution in this portion of the sample. A region of higher zirconium content close to the zirconium area has such a fine eutectoid structure that it was not resolved and appears as a dark band. There was a thin band between this dark area and the zirconium which differed very slightly in appearance from the original zirconium. This probably represents the solubility of uranium in alpha zirconium. No evidence of the two-phase region above 605° C on the zirconium side of the phase diagram was observed.

In an attempt to prepare a 50 per cent alloy by melting uranium with Bureau of Mines sponge zirconium in a thoria crucible an interesting

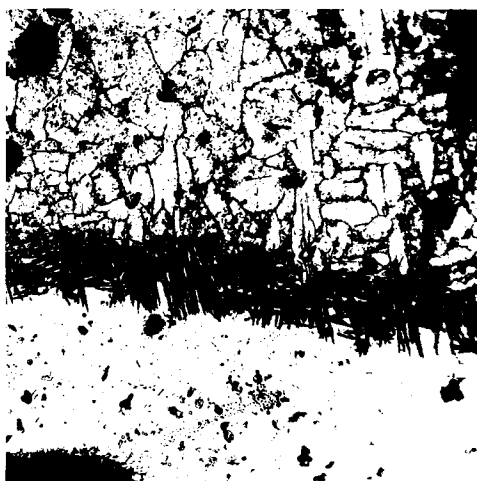
concentration gradient sample was made. The crucible containing the two metals was heated slowly to  $1725^{\circ}\text{C}$  and then cooled slowly to avoid breaking the thoria crucible by thermal shock. Not all of the zirconium had gone into solution and a section of the sample, when polished and etched, revealed chunks of zirconium floating in an inhomogeneous matrix. During solidification, dendrites of higher zirconium content were formed and the sample evidently did not become homogeneous while being cooled through the solid solution region. These dendrites had a composition slightly above 30 per cent zirconium and the liquid between them had slightly less than 30 per cent zirconium. As a result of this lack of equilibrium, a sample quenched at  $650^{\circ}\text{C}$  showed no  $683^{\circ}\text{C}$  eutectoid structure in the dendrites but the area between the dendrites did show this eutectoid. The microstructure of this quenched sample is shown in Figure 83 where the dendrites appear as light areas in a dark eutectoid background. The formation of these alloyed dendrites is evidence of a solid solution in the system. Figure 84 is a photomicrograph taken at higher magnification and shows the interface between zirconium and the melt in this sample as quenched from  $650^{\circ}\text{C}$ . The  $683^{\circ}\text{C}$  eutectoid of the uranium-rich areas shows as large dark patches. The band between the zirconium, shown at the top in the figure, and the relatively clear gamma-beta solid solution contains needles similar to these found in the alpha zirconium plus gamma-beta solid solution two-phase region of the diagram. The clear gamma-beta solid solution region in this sample might in the



82



83



84

Figure 82 - Zirconium-uranium diffusion band. Heated to 1200° C and slow-cooled. Phosphoric acid elec. etch. X 250.

Figure 83 - Zirconium-uranium alloy. Quenched from 650° C. Zirconium-rich dendrites in uranium-rich matrix. Nitric acid base etch. X 75.

Figure 84 - Zirconium-uranium diffusion band. Quenched from 650° C. Zirconium on top. Nitric acid base etch. X 250.

absence of X-ray data be mistaken for an intermetallic compound.

The structures found in the diffusion band samples could be identified and related to the phase diagram. They were useful in making a preliminary survey and were a degree of assurance that no major phase areas were overlooked in studying the system. They also indicate that equilibrium is rather slowly established in the gamma-beta solid solution area and that zirconium does not dissolve rapidly in molten uranium at temperatures of about 100° C below its melting point.

### C. X-ray Diffraction Data

The application of X-ray diffraction studies to this investigation was limited to the identification of phases. The X-ray powder diagram of uranium is so complex that determination of solid solubility limits or even the detection of solid solubility by changes in the lattice dimensions is almost an impossible task. The powder diagram of zirconium is more easily handled and accurate lattice measurements can be made. However, the effective atomic diameters of uranium and zirconium differ so little that a large amount of solid solubility could still be undetected by X-ray methods. The closest atomic approach of zirconium atoms in the hexagonal form is 3.16 Å and in the body centered cubic form is 3.12 Å. The closest atomic approach for gamma uranium calculated from the lattice constant of 3.48 Å is 3.02 Å. Assuming the alloys obeyed Vegard's law, as much as 10 atomic per cent solid solubility would only change the body centered

cubic lattice constant by only  $0.01 \text{ \AA}$ . Since determination of the lattice constant of even a cubic lattice to a greater accuracy than  $\pm 0.005 \text{ \AA}$  is difficult, it is evident that X-ray diffraction is quite an insensitive method of determining solid solubility in this case. The complexity of exact lattice constant determination of hexagonal lattices is a further limitation of the X-ray method. The lattice constants of alpha zirconium increase with an increase in the amount of oxygen dissolved in the zirconium and even the most precise lattice constant determinations would have been useless unless the oxygen content of the sample could have been accurately determined.

The X-ray diffraction patterns of alpha uranium, alpha zirconium and of 30.10, 52.24 and 72.22 per cent zirconium alloys as slowly cooled to room temperature are shown in Figures 85 through 89. The lines appearing in the alloy X-ray patterns could all be accounted for as belonging to either alpha uranium or alpha zirconium. This was taken as very good evidence that there were no intermetallic compounds at room temperature. The lattice constants of alpha zirconium calculated from a powder diagram of Bureau of Mines sponge were  $a = 3.212 \pm 0.015 \text{ \AA}$  and  $c = 5.13 \pm 0.03 \text{ \AA}$ . These are in quite good agreement with the literature values of  $a = 3.228 \text{ \AA}$  and  $c = 5.120 \text{ \AA}$  which were determined from zirconium prepared by the iodide hot wire method. The difference in method of preparation of the zirconium and the resulting difference in purity might account for the variation in observed lattice parameters. The lattice constants for the hexagonal closest-packed phase appearing in the 72.22 per cent



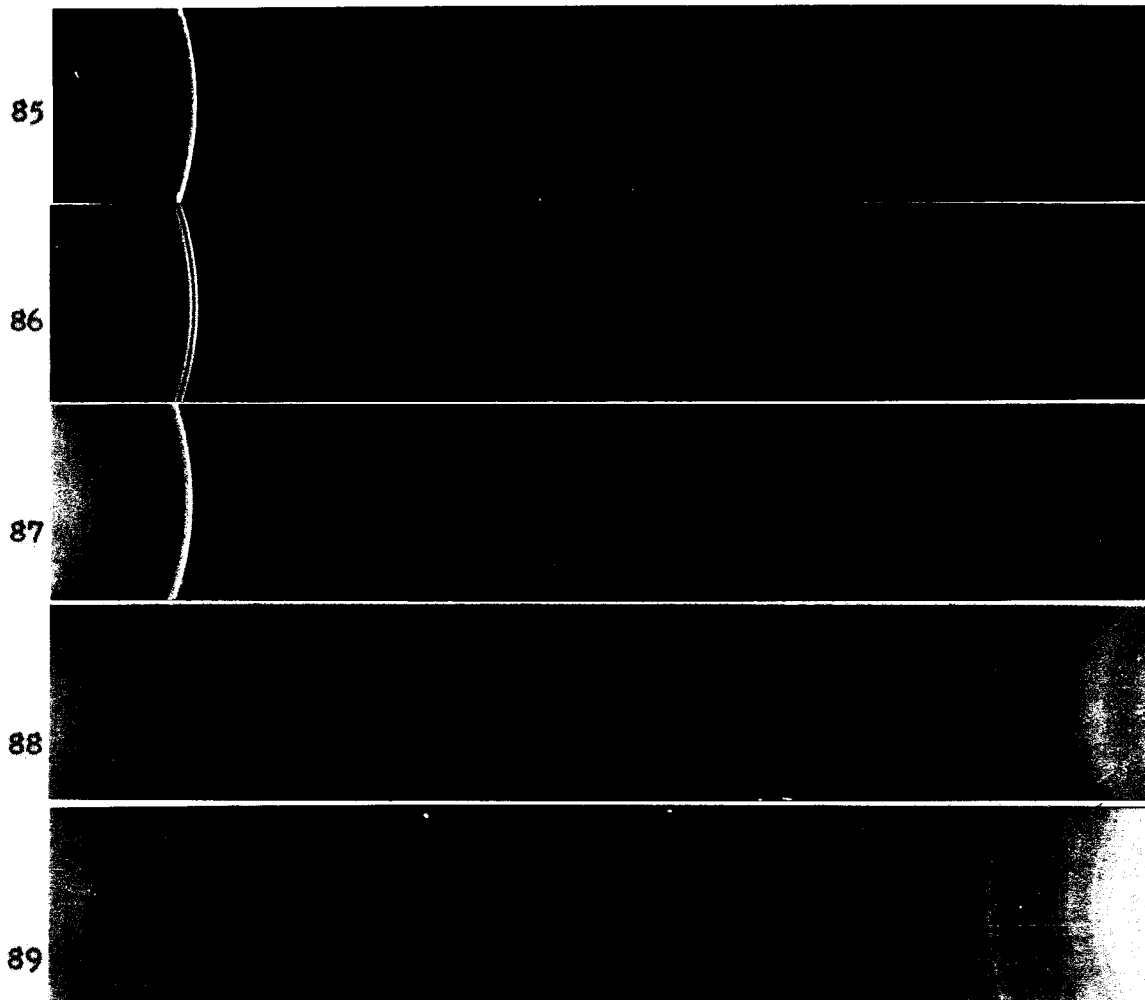


Figure 85 - Alpha zirconium, Bureau of Mines sponge.

Figure 86 - 72.22% zirconium. Slow-cooled.

Figure 87 - 52.24% zirconium. Slow-cooled.

Figure 88 - 30.10% zirconium. Slow cooled.

Figure 89 - Alpha uranium.

11.4 cm camera. Filtered copper radiation.

zirconium alloy were determined. The observed values were  $a = 3.218 \pm 0.015 \text{ \AA}$  and  $c = 5.140 \pm 0.03 \text{ \AA}$ . These values agree within experimental error with the literature values and the constants measured on Bureau of Mines sponge zirconium.

The attempts to hold high temperature crystal structures by quenching alloys from an elevated temperature were all unsuccessful. In one experiment filings of the alloys containing 29.45, 52.24 and 72.22 per cent zirconium were heated at  $800^{\circ} \text{C}$  for 36 hours and then quenched in water. The X-ray diffraction patterns which were obtained are shown with the patterns of alpha uranium and alpha zirconium in Figure 90 through 94. Practically all of the lines may be identified as belonging to alpha uranium or alpha zirconium. These alloys quenched from this temperature appear to consist of a single phase when examined under the microscope and according to the phase diagram if, the quench had retained a single phase, no alpha uranium or alpha zirconium should have been present. Evidently the high temperature crystal structure transformed to the forms which are stable at room temperature in spite of being quenched and without causing a detectable change in the microstructure. The lattice constants of the hexagonal closest-packed phase in these quenched samples were larger than in the slow-cooled samples. The measured values from the quenched 72.22 per cent alloy were  $a = 3.248$  and  $c = 5.190 \text{ \AA}$ . This change from the slow-cooled values is greater than the experimental error and was quite constant for all three quenched

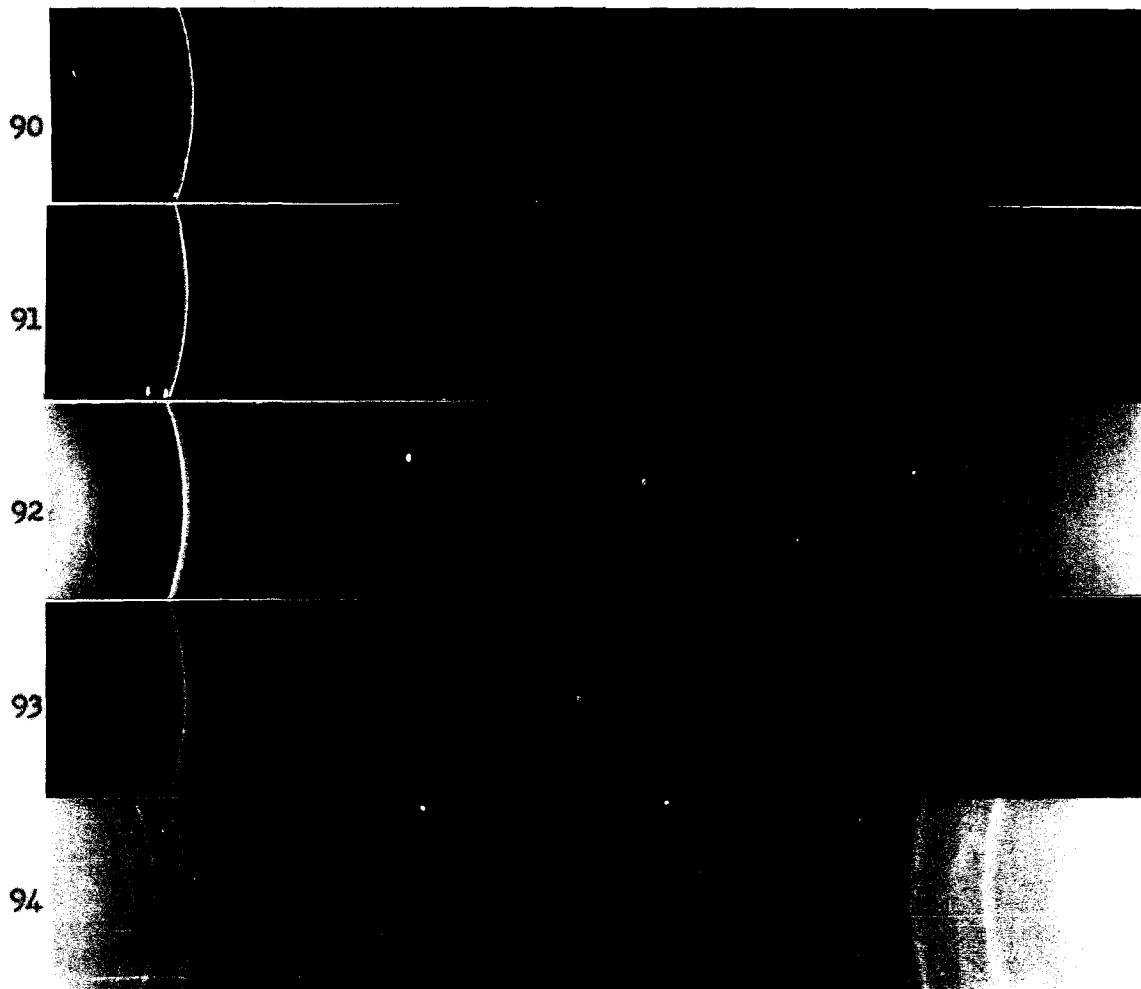


Figure 90 - Alpha zirconium, Bureau of Mines sponge.

Figure 91 - 72.22% zirconium. Quenched from 800° C.

Figure 92 - 52.24% zirconium. Quenched from 800° C.

Figure 93 - 29.45% zirconium. Quenched from 800° C.

Figure 94 - Alpha uranium.

11.4 cm camera. Filtered copper radiation.

alloys. According to the diagram no alpha zirconium should have been present in these alloys when they were at  $800^{\circ}\text{C}$  therefore, the alpha zirconium must have been formed during or after quenching. If this were supersaturated alpha zirconium the smaller size of the uranium atoms should have caused a shrinking of the lattice. Oxygen dissolved in zirconium causes an expansion of the hexagonal lattice which varies with the oxygen content. Since all three alloys had almost the same lattice constants, if the expansion of the lattice was due to oxygen then the same concentration must have been present in all of these. This would appear to be a somewhat unlikely coincidence. The explanation might be that the alpha zirconium lattice is strained as a result of the rapid cooling and precipitation of uranium which occurred during the quench.

The examination by X-ray diffraction of alloys of uranium and zirconium prepared in this laboratory has indicated that alpha uranium and alpha zirconium were present in all alloys at room temperature. The high temperature crystal structures were not preserved by quenching to room temperature in water. There was no X-ray evidence of the existence of intermetallic compounds at room temperature. These results do not agree with the work of Kaufman and co-workers who reported that the body-centered cubic phase may be held by quenching alloys from above  $600^{\circ}\text{C}$  and that a body centered tetragonal form exists below  $600^{\circ}\text{C}$ . The alloys with which they were working were prepared by a different method and from different zirconium metal. A small amount of an impurity might have caused the transformation precipitation

to be sluggish in the one case or to be rapid in alloys in which the cubic phase was not held by quenching. The body-centered cubic phase above 600° C agrees with the phase diagram as drawn and the body-centered tetragonal phase might be a transition structure similar to the reported metastable tetragonal martensite of some quenched steels.

#### D. Hardness and Working Properties

The hardness of uranium-zirconium alloys was measured on slow-cooled and on quenched samples. The Rockwell A scale was used, at least three readings taken for each specimen and the results averaged. A tabulation of the results is given in Tables 3 and 4.

The addition of zirconium to uranium causes an increase in the hardness of the alloy in the slow-cooled condition. The hardness increases with the amount of zirconium up to about 16 per cent zirconium and then begins to decrease slightly. Since the solubility of zirconium in alpha uranium is less than 0.57 per cent at room temperature, this increase in hardness must be due to the finely dispersed 683° C eutectoid structure and the small grain size.

The alloys containing less than 40 per cent zirconium were hardened by heating above 683° C and quenching. The hardness produced was the same if the sample was heated just a few degrees above 683° C or if it was heated to 800° or 900° C and quenched. The maximum hardness of the quenched alloys increased with the concentration of zirconium up to 4.75 per cent. Above this composition it

TABLE 3

Hardness of Uranium-Zirconium Alloys Prepared in Dolomitic Oxide

(Rockwell A Scale)

Composition Wt. % Zr	Slow Cooled	Temperature Quenched from, in degrees Cent.							
		580	614	657	678	694	700	800	900
Pure U	45 - 52								
0.57	53	53	55	55	58	58		59	
1.18	57	56	59	59	55	62	60	60	
1.88	59	59	58	58	56	64	67	67	
4.75	63	65	61	61	61	66	73	75	
5.43						78	75		
7.62						73	75		
7.90						75	75		
9.29						74	76		
9.42					61		76		
15%		69	62			72	74		75
25%			62				66		
30%		68	60				69		70
50%		61	61				60		61
75%	71	68	66				70		72
90%		72	72						71
100	65								

TABLE 4

Hardness of Uranium-Zirconium Alloys Prepared in Graphite Liners  
(Rockwell A Scale)

Composition Wt. % Zr	Slow Cooled	Temperature quenched from, in degrees Cent.					
		580	630	700	800	900	1000
29.45					70		
39.40		64	57	58		59	
52.24		61		59	61	61	
72.22		61	69	71	70	72	
87.30		58	55	63	65	68	68
94.30	63	65	65	66	67	65	64
97.20							59
100	45 - 50						
30.10 <sup>a</sup>		68	59	65	68		
40.30 <sup>a</sup>		64	57	58	57		
48.95 <sup>a</sup>		64	58	58	57		
60 <sup>a</sup>		64	60	60	65		
90 <sup>a</sup>		57	57	60	63		
100 <sup>a</sup>	38 - 42						

<sup>a</sup> Alloys prepared by arc melting uranium and zirconium

was quite constant through 30.10 per cent. Quenching the same alloys from just below  $683^{\circ}\text{C}$  did not increase the hardness as compared to those slow-cooled and in the 15.45 and 30.10 per cent compositions resulted in a slight softening. The hardening evidently results from quenching through the  $683^{\circ}\text{C}$  eutectoid transformation. Since the beta or gamma form of uranium was not retained by quenching, the hardness may arise from formation of either strained or supersaturated alpha uranium or from the submicroscopic precipitation of zirconium.

Additions of uranium to zirconium caused an increase in hardness of the high zirconium alloys. The hardness of a slow-cooled sample was about the same as that of the sample quenched from below  $605^{\circ}\text{C}$ . Heating the alloys slightly above  $605^{\circ}\text{C}$  and quenching resulted in an appreciable decrease in hardness for most of the alloys from 90 per cent zirconium to 4.75 per cent zirconium. Quenching from  $700^{\circ}\text{C}$  and higher temperatures caused some increase in the hardness of the alloys containing more than 52.24 per cent zirconium.

The alloys of high zirconium content which were prepared by bomb reduction in dolomitic oxide liners were consistently harder than alloys of the same uranium to zirconium ratio which were prepared by bomb reduction in graphite liners or by arc melting. The reason for this was probably the presence of more oxygen in solid solution in the metal. The hardness of zirconium alloys of the same uranium-zirconium ratio prepared by arc melting and by bomb reduction



in graphite liners was the same in most of the alloys. The arc melted samples showed little variation in hardness but some of the bomb reduced alloys were harder and some were softer than the corresponding arc melted alloys. This indicated that the oxygen contamination of the bomb reduced metal varied from sample to sample. Since some of the bomb reduced alloys were softer than the arc melted alloys they must have contained less oxygen.

With the exception of alloys containing from 90 to 100 per cent zirconium, the alloys of uranium and zirconium do not show much ductility at room temperature. They are quite brittle and can not be cold worked to any extent by rolling. The 90 per cent alloy prepared by arc melting was rolled at room temperature to 60 per cent reduction in thickness before starting to crack. Attempts to cold work alloys containing more than 10 per cent uranium resulted in severe cracking and fracture after a few per cent reduction. The 40.30 and 60 per cent zirconium alloys were hot rolled at 700° C to sheet which was 0.016 inches thick starting with 0.25 inch thick bar. All rolling was done without cladding or protection from oxidation. A dense adherant black film was formed on the hot-rolled metal but could be removed by pickling in dilute hydrofluoric acid.

#### E. Discussion of Alloy Preparation

The bomb reduction method has proven to be quite satisfactory for the production of alloys of uranium and zirconium. The homogeneity of the alloys was very good as would be expected from the intimate

mixing of the finely ground fluorides used as starting materials. The uranium-zirconium ratio of the alloys as determined by chemical analysis was always very close to the ratio of these in the charge. The deviations of the constituents from the composition which was calculated from the amounts of the respective fluorides in each charge are shown in Table 5. The yield of alloy from this method was from 93 to 98 per cent when dolomitic oxide liners were used.

Until quite recently the zirconium metal produced in oxide liners was quite hard and brittle. This was also true of the uranium-zirconium alloys containing more than 15 per cent zirconium. Walsh<sup>38</sup> has reported that recent work on bomb reduction of zinc-zirconium alloys in calcium oxide or dolomitic oxide has resulted in softer zirconium metal than that previously obtained and that it may be possible with such liners to produce metal approaching the softness and ductility of Bureau of Mines cast ingot zirconium. If this can be done then it might become practical to prepare uranium-zirconium alloys by bomb reduction in oxide liners. This would make the use of graphite liners, which are expensive and give reduced yields, unnecessary.

The alloys which were prepared in graphite liners compared quite well in the arc melted alloys in softness. The amount of carbon in the alloys made in graphite liners was considerably greater than in arc melted samples but this did not appear to harden the samples and for some purposes might not be harmful.

TABLE 5

Chemical Analysis of Uranium-Zirconium Alloys

(Alloys prepared in dolomitic oxide liners except where otherwise noted.)

Per cent Zirconium in charge			Per cent by Weight			Total
	U	Zr	Fe	C	N	
0.5	98.71	0.57				
1.0	96.15	1.18	0.011	0.048	0.12	97.57
2.0	97.11	1.88				
5.0	94.30	4.75	0.026	0.071	0.32	99.47
6.0	92.63	5.43				
7.0	89.05	7.90				
8.0	89.55	7.62				
9.0	88.35	9.29				
10.0	89.15	9.42	0.025	0.090	0.18	98.87
15 <sup>a</sup>	81.15	14.57	0.009	0.055	0.15	95.94
15 <sup>a</sup>	82.86	15.98	0.021	0.078	0.26	99.20
30 <sup>a</sup>	67.60	28.65	0.026	0.330	0.16	96.61
30 <sup>a</sup>	68.41	29.45	0.052	0.128		98.04
30 <sup>b</sup>	69.47	30.10	0.001	0.034	0.02	99.64
40 <sup>b</sup>	59.50	40.30	0.017	0.034	0.02	99.85
40 <sup>a</sup>	61.00	39.40	0.016	0.155	0.025	100.60
50 <sup>b</sup>	50.40	48.95	0.007	0.035	0.02	99.39
50 <sup>a</sup>	47.50	51.20	0.020	0.834	0.117	99.77
50 <sup>a</sup>	46.01	52.24	0.0966	0.083	0.246	98.67
50	47.40	36.3				
60 <sup>a</sup>	38.80	60.35	0.013	0.178	0.140	
75 <sup>a</sup>	24.53	72.22	0.133	0.105	0.188	97.18
90 <sup>a</sup>	10.05	87.30	0.092	0.155	0.139	97.77
95	4.41	94.30	0.180	0.535	0.098	99.52
98 <sup>a</sup>	2.32	97.20	0.026		0.024	99.57
100 <sup>a</sup>				0.042		
100				0.142		

<sup>a</sup> Alloys prepared by bomb reduction in graphite liner

<sup>b</sup> Alloys prepared by arc melting zirconium and uranium

Analytical results on many of the alloys which were prepared are given in Table 5. The relatively large amount of iron present in the higher zirconium alloys was due to the method of grinding the zirconium tetrafluoride used in the reduction. This could be lowered by a factor of ten if a method of grinding the fluoride which did not introduce iron had been used. The nitrogen content of these alloys was surprisingly high since both uranium and zirconium with less 0.03 per cent nitrogen can be produced by bomb reduction. No reason for this amount of nitrogen contamination was found.

The arc melting method of preparing uranium-zirconium alloys had several advantages over bomb reduction. The carbon content of the alloys prepared by this method was lower than in alloys prepared by reduction in graphite. The samples were free from the slag inclusions and blow holes which most of the bomb reduced metal contained. This was not an important difference in the preparation of alloys for thermal analysis and phase identification but would be important in corrosion results or the fabrication of nuclear fuel elements. The amount of metal which was lost as dross was very low which would be an advantage if working with fissionable material.

This method requires zirconium metal as a starting material and the quality of the alloy depends on the purity of the starting materials. The equipment necessary is somewhat expensive and rather difficult to adapt to production of large billets of uniform alloy composition. The main portion of the alloys prepared by arc melting

were homogeneous but the surface in contact with the crucible often varied in composition from the major portion. This would be a disadvantage in fabrication and would require the removal of these surfaces of the ingot.

## V. SUMMARY

Alloys of uranium with zirconium were prepared by bomb reduction of uranium and zirconium tetrafluorides in dolomitic oxide liners and in graphite liners. Alloys of uranium with zirconium were also prepared by other methods such as powder metallurgy, melting uranium with zirconium in graphite, and arc melting uranium with zirconium. These alloys were studied by thermal analysis and by observation of the first sign of melting. Microscopic examination of slow-cooled and of quenched alloys was used to investigate the nature of the various phase fields. The phases which were present in the alloys were identified by their X-ray diffraction patterns. The hardness of the alloys was measured and their ability to undergo mechanical working was investigated.

A phase diagram was proposed for the uranium-zirconium system. The liquidus and solidus lines have no maximum, minimum or horizontal portion. A continuous solid solution exists between gamma uranium and beta zirconium. The solubility of zirconium in alpha uranium is less than 0.57 per cent at  $579^{\circ}\text{C}$ . The solubility in beta uranium is less than 1.18 per cent at  $694^{\circ}\text{C}$ . A eutectoid transformation takes place at  $683^{\circ}\text{C}$ . The solubility of uranium in alpha zirconium is probably between 2.3 and 4.4 per cent at  $580^{\circ}\text{C}$ . A thermal arrest at  $605^{\circ}\text{C}$  was observed for alloys from 5 per cent zirconium to 95 per cent zirconium. This was interpreted as a second eutectoid transformation. X-ray diffraction data indicated that alpha uranium and alpha zirconium were present at room temperature in all alloy compositions studied.

## VI. BIBLIOGRAPHY

1. "Project Handbook" Vol. III, Chapt. IX, Classified Publication, Atomic Energy Comm. (1946).
2. Suits, C. G. and K. H. Kingdon, KAPL-276, Classified Report, Atomic Energy Comm. (Dec. 1949).
3. Rayner, G. V., UAC-7, Classified, (Jan. 1949).
4. Boulger, F. W., BMI-10, Declassified Report, Atomic Energy Comm. (Mar. 1948).
5. Burgers, W. C., Z. anorg. allg. chem. 205, 81-86 (1932).
6. Buzzard, R. W., and H. E. Cleaves, TID-65, Classified, (July 1948).
7. Seybolt, A. U., LA-42, Classified, (Nov. 1943).
8. \_\_\_\_\_, LA-68, Classified, (Feb. 1944).
9. \_\_\_\_\_, LA-69, Classified, (Mar. 1944).
10. Chipman, J., CT-2387, Classified, (Nov. 1944).
11. Cohen, M. and J. Chipman, CT-2472, Classified, (Dec. 1944).
12. Cohen, M., CT-2619, Classified, (Jan. 1945).
13. Cohen, M. and J. Chipman, CT-2699, Classified, (Feb. 1945).
14. Cohen, M., CT-2780, Classified, (Mar. 1945).
15. \_\_\_\_\_, CT-2606, Classified, (April 1945).
16. \_\_\_\_\_, CT-2997, Classified, (May 1945).
17. \_\_\_\_\_, CT-3060, Classified, (June 1945).
18. \_\_\_\_\_, CT-3194, Classified, (July 1945).
19. Kaufmann, A. R., MIT-1004, Classified, (May 1948).
20. \_\_\_\_\_, MIT-1029, Classified, (Sept. 1949).
21. \_\_\_\_\_, MIT-1034, Classified, (Oct. 1949).
22. \_\_\_\_\_, MIT-1040, Classified, (Feb. 1950).

23. \_\_\_\_\_, MIT-1045, Classified, (May 1950).
24. Sutton, C. R., ANL-HE646, Classified, (June 1950).
25. Greninger, A. B., CT-2616, Classified, (Jan. 1945).
26. \_\_\_\_\_, CT-2668, Classified, (Feb. 1945).
27. Foote, F., CT-2857, Classified, (Mar. 1945).
28. Greninger, A. B., CT-2925, Classified, (April 1945).
29. Russel, H. W., BMI-P-12, Classified, (Jan. 1949).
30. Boer, J. H. De and J. D. Fast, Electrolysis of Solid Solutions of Oxygen in Metallic Zirconium. Rec. Trav. Chim. 59, 161-167 (1940).
31. Angier, R. P., and H. H. Hausner, SEP-28, Classified, (Dec. 1949).
32. Angier, R. P., and H. H. Hausner, NYO-1127, Classified Report, Atomic Energy Comm. (April 1950).
33. Spedding, F. H. and others, CT-M-2949, Classified, (Sept. 1945).
34. Walsh, K. A., ISC-94, Classified, (1950).
35. Chiotti, P., ISC-103, Classified, (1950).
36. Forsythe, Optical Pyrometers, J. Optical Soc. Am. 10, 19-37 (1925).
37. Boer, J. H. De and J. D. Fast, Influence of Oxygen and Nitrogen on Alpha-beta Transition of Zirconium. Rec. Trav. Chim. 55, 459-467 (1936).
38. Walsh, K. A., [Classified Unpublished Research 7], Ames Laboratory of Atomic Energy Comm. (1950).



## VII. ACKNOWLEDGMENTS

The author wishes to express his sincere thanks to Dr. H. A. Wilhelm for his encouragement and counsel and to Mr. M. A. Schoenbeck and Mr. R. Russi for their capable and cooperative assistance in the experimental work. In addition, acknowledgment is made to the members of the analytical group who under the direction of Dr. C. V. Banks performed the necessary analyses and to the many other members of the Ames Laboratory who have given assistance and advice. Gratitude must be expressed for the funds and facilities made available for the research by the Ames Laboratory of the Atomic Energy Commission.